7   Molecular Electronics

Molecular electronics is presently concerned with the examination of organic materials in the desire to determine their applicability to the storage, transfer, and processing of information. A possible technically useful property is the greater miniaturization attainable with organic materials in comparison to inorganic semiconductors. It is however questionable whether this miniaturization can ever be achieved.

7.1   Molecular Conductors

The polyacetylene mentioned in chapter 6 belongs to the molecular conductors, as does the biological substance ß-Carotene, in which in a carbon chain, single and double bonds alternate. Defects are necessary for the conductivity in the direction of the chain of such polymers. These can be created by the addition of an oxidizing agent such as $FeCl_3$ (doping with an electron donor), or by breaking a double bond. Doped polyacetylene has a conductivity which is only one order of magnitude below that of a good metallic conductor.

Organic metals are crystalline bonds composed of an electron donor and an electron acceptor, usually arranged in stacks. There is a conductivity along the stack if charge transport occurs due to overlapping of the π-orbitals of neighbouring molecules. The radical anionic salt dicyanochinon-diimine (DCNQI) with a free metallic substituent group (e.g. $-CH_3$, Cl, Br, I) or counterion of the salt (e.g. Cu, Ag, Li) acts like a metal-similar semiconductor or a one-dimensional conductor. With CH_3-groups at these positions, the conductivity at low temperatures reaches that of copper at room temperature. Apparently there are increased inter-stack charge transfers between Cu and the CN groups. Figures were taken from Haken and Wolf.

Fig. 21.2. The temperature-dependent electrical conductivity of some Cu salts of DCNQI. The compounds differ in the nature of the substituents on the DCNQI molecules; cf. Fig. 21.1. Me– refers to a –CH₃ group (methyl), while I or Br are iodine or bromine atoms as substituents in place of the methyl groups; compare the molecular structure in Fig. 21.1. The crystal structures are very similar in each case. The conductivity ranges from that of an organic metal even down to very low temperatures (*uppermost curve*) to that of a metal-like semiconductor (the two *lowest curves*; one of them is for an alloy). [From H.C. Wolf, Nachr. Chem. Techn, **37**, 350 (1989)]
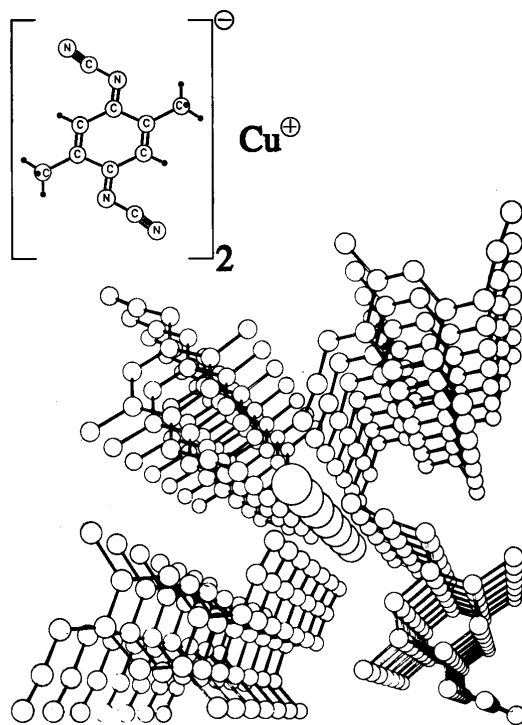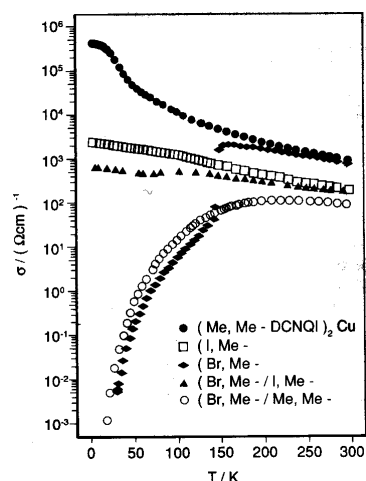
Fig. 21.1. The crystal structure of the radical-anion salt 2,5 dimethyl- dicyanoquinone-diimine (DCNQI), with copper as its inorganic partner. In the centre of the picture, a chain of Cu ions can be seen; they are, however, not responsible for the metallic conductivity of the material. Around them are four stacks of the organic partner molecules. Conductivity takes place along these stacks. The stacks are joined together via –CN groups through the central Cu, so that the one-dimensionality is somewhat reduced. [After P. Erk, S. Hünig, J.U. v. Schütz, H.P. Werner, and H.C. Wolf, Angew. Chem. **100**, 286 (1988)]. The molecular structure diagram at the upper left shows the H atoms as dots only

7.2 Molecular Switching Elements

We have photochromism, if a molecule in state A changes to state B by the interaction with light of wavelength l_A, and goes back into state A by interaction with light of wavelength l_B. An example of such a bistable molecule with two valence isomers (the π-bond is changed into a σ-bond by ring formation) is the thiophene fulgide. The ring state contains a chain of conjugated double bonds which is colourful and can serve the transport of energy, e.g. oriented transport of excitement energy between the donator and acceptor of energy.
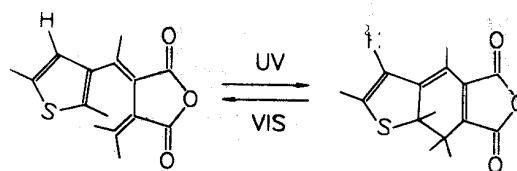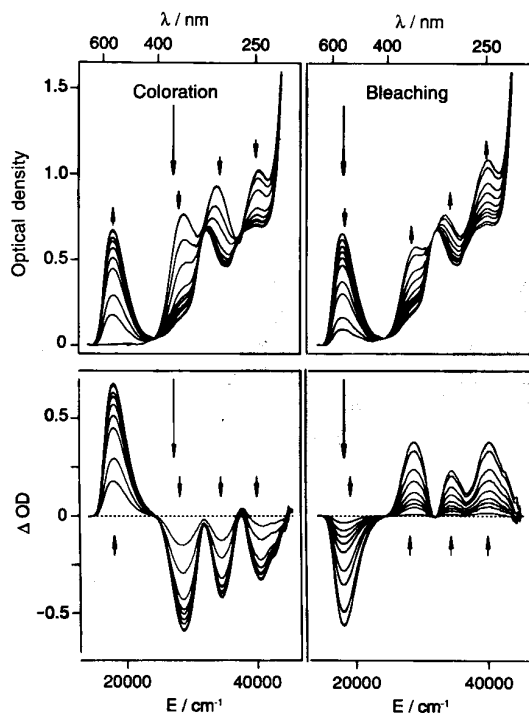

Fig. 21.4. Molecules as switches: the thiophene fulgide molecule is photochromic and can be reversibly switched between the two valence-isomeric configurations shown. (The dashes on C atoms in the figure indicate CH_3 groups)
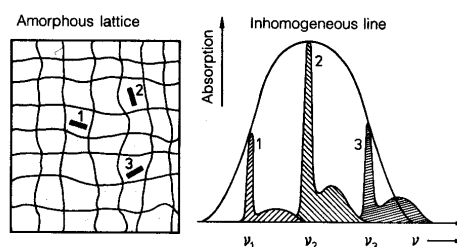
Fig. 21.5. Colouration and bleaching of the thiophene fulgide molecule (in solution), as shown in Fig. 21.4. *Upper part*: the optical density. *Lower part*: changes in the optical density through the effect of light with the wavelength indicated by the arrows. [From H.C. Wolf, Nachr. Chem. Techn. **37**, 350 (1989)]

All figures on this page were taken from Haken and Wolf.

7.3 Molecular Storage

The most promising process for the production of molecular storage is that of "hole burning". It is based on the difference between homogenous and inhomogeneous broadening of a spectral line. The homogenous broadening is determined by the lifetime of the states which take part in the transitions. In addition to the homogenous broadening there is the inhomogeneous broadening,

Fig. 21.9. The inhomogeneous broadening of molecular spectral lines .in a matrix; this is the basis for the phenomenon of hole-burning. In an amorphous matrix, the electronic excitation energies and thus the transition frequencies of molecules are distributed over a range of energies, because the individual molecules have differing local environments (*left side*). Each individual configuration has a particular absorption spectrum, consisting of a zero-phonon line and phonon sidebands. The overall absorption is a superposition of all these individual absorption spectra (*right side*). [After D. Haarer, Angew. Chem. **96**, 96 (1984)]
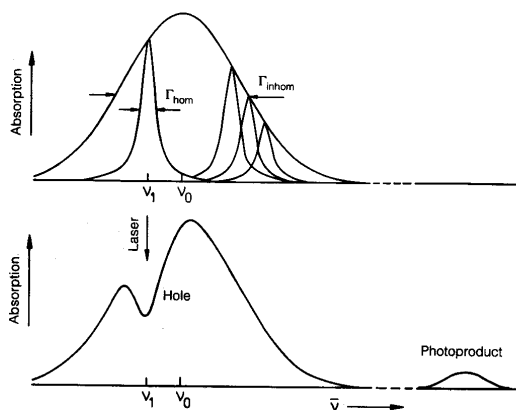

which is be caused by the motion of the particle (Doppler broadening), differing intermolecular or master-slave interactions, and other mechanisms. An experimentally approachable definition of homogenous and inhomogeneous broadening is: in an inhomogeneously broadened spectral line, it is possible with intensive radiation (e.g. a laser) to burn a hole whose width is the natural line width. This hole burning is caused by the partial saturation of the spectral line. If, however, the radiation causes the rearrangement of a bond in the molecule, we have photochemical hole burning. That includes photoisomerization.

Fig. 21.10. Photochemical hole-burning: laser light of a narrow bandwidth is used to irradiate an inhomogeneously broadened spectral line. This burns a hole into the absorption line, having the width of the laser bandwidth or the homogeneous linewidth Γ_{hom} of the individual molecules. The absorption line of the photoproduct appears at some other point in the spectrum. [After S. Völker, Ann. Rev. Phys. Chem. **40**, 499 (1989)]
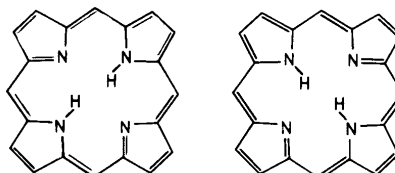

Fig. 21.11. In the porphine molecule (free base form), the two central H atoms can be switched back and forth between two configurations by the action of light (photoisomerisation). In solid solutions, this leads to a "hole" in the absorption spectrum. Optical hole-burning with organic molecules was first investigated in this system. The photoisomerisation is observed only at low temperatures; at room temperature, the central protons can move freely between the two configurations, as can be demonstrated by proton spin resonance experiments
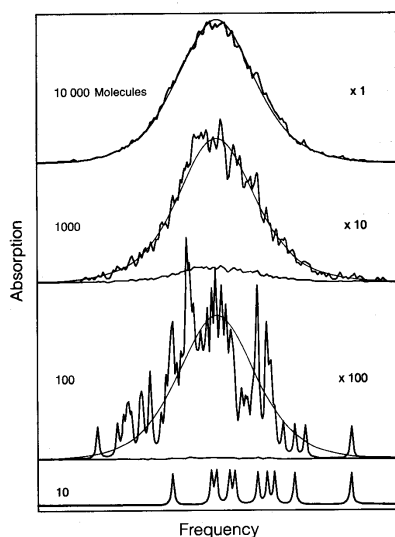

Fig. 21.12. The simulated absorption spectra of N molecules in a disordered matrix. As N decreases from 10 000 to 10, the integral absorption also decreases; this is the reason for the magnification factors shown at the right. The ratio of homogeneous to inhomogeneous linewidths has been assumed here to be 1:40. In reality, for glass matrices it has values of $1:10^4$ to $1:10^6$ at homogeneous linewidths of 10^{-1} to 10^{-3} cm^{-1} and an inhomogeneous linewidth of 10^3 cm^{-1}

7.4 Spectroscopy of a Single Pentacene Molecule

In molecular electronics, individual molecules play a role. It is therefore desirable to spectroscopically examine such individual molecules in the condensed phase.

This has since been achieved by several methods. An example is the fluorescence excitation of individual pentacene molecules

All figures on this page were taken from Haken and Wolf.
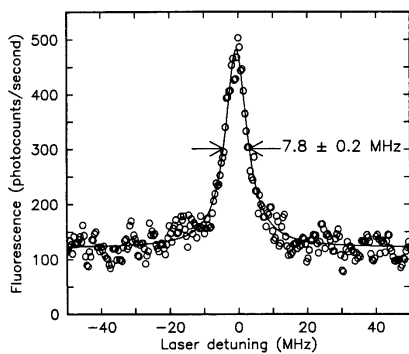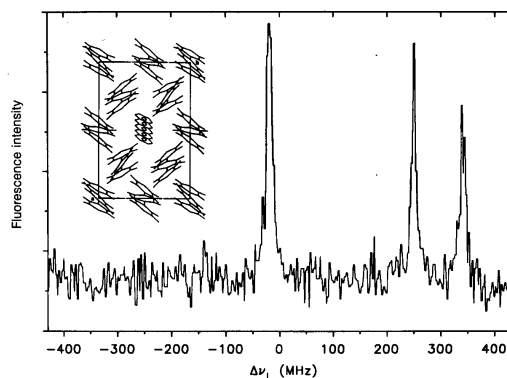

Fig. 21.13. The fluorescence excitation spectrum of a single pentacene molecule in a thin p-terphenyl crystal at 1.5 K, concentration $8 \cdot 10^{-9}$ mol/mol = $1.7 \cdot 10^{13}$ cm^{-3}. The centre, at 0 MHz, corresponds to an absorption wavelength of 592.407 nm. From W.P. Amrose, Th. Basché, and W.E. Moerner, J. Chem. Phys. **95**, 7150 (1991). See also W.E. Moerner and Th. Basché, Angew. Chem. **105**, 537 (1993)

Fig. 21.14. The fluorescence excitation spectrum of three individual pentacene molecules in p-terphenyl, showing the crystal structure of the host as an inset. The abscissa value 0 MHz corresponds to a wavelength of 592.362 nm. The fluorescence intensity is plotted as a function of the wavelength of the extremely narrow-band excitation light. Kindly provided by C. Bräuchle and Th. Basché

7.5 Single molecule polarization measurement on a light harvesting complex

Carsten Tietz, Uwe Gerken, Fedor Jelezko and Jörg Wrachtrup: Polarization Measurements on Single Pigment-Protein Complexes, Single Mol. 1 (2000) 1, 67-72

Individual antenna complexes from different photosynthetic units have been investigated by single molecule spectroscopy. In such energy transfer systems the polarization of the fluorescence emission gives valuable information about the nature of the emitting state, which is not readily available with other methods like fluorescence excitation or emission spectroscopy. The peripheral antenna light harvesting complex from purple bacterium Rhodopseudomonas Acidophila shows predominantly linear polarized fluorescence emission at low temperature, whereas at room temperature the fluorescence is randomly polarized. This is attributed to the fact, that at low temperature in the fluorescence emitting state the excitation energy is localized mainly on 4-5 chromophores. Analysis of the fluorescence emission of single peripheral antenna complexes of green plants indicate that for trimers of this species more than one Chlorophyll is responsible for the final fluorescence emission, which points towards a weak intermonomer coupling in the complex.

Answering how many molecules finally receive the excitation energy provides a way to understand how nature optimizes transfer among different units of the photosynthetic apparatus. From the time averaged isotropic fluorescence polarization of LH2 it can be concluded, that a rapid randomization of trapping sites in the B850 occurs. At low temperature an inhomogenous distribution of eigenenergies around 200 cm-1 has been found. Possibly fluctuations at room temperature result in larger eigenenergy variations with a concomitant trapping at random sites in the ring. Stepwise photobleaching in LHCII trimers suggests, that there is weak intermonomer coupling in this system. Although up to five molecules could be responsible for fluorescence emission in LHCII monomers, a single step is found in photobleaching. Possibly trap formation in a system of coupled chlorophylls explains this observation.

Fig. 3. Confocal image of a single LH2 at room temperature with a two detector set-up. The right part of the figure shows a line scan across the complex. The two traces represent the fluorescence intensity in the two detector channels.

Fig. 4. Fluorescence intensity trace of a single LHCII modulated by a polarizer in front of the detector. The trace has been recorded at room temperature.

The figures above were taken from the reference given at the top of this page.