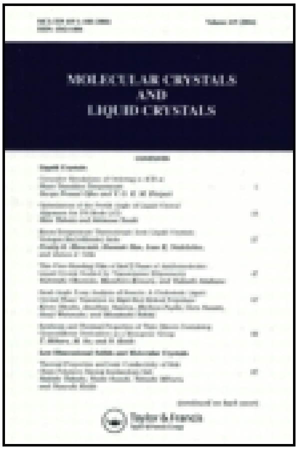

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Studies of Organic Semiconductors for 40 Years—VII

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Version of record first published: 06 Dec 2006.

To cite this article: Z. D. Popović (1989): Studies of Organic Semiconductors for 40 Years—VII, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 171:1, 103-116

To link to this article: http://dx.doi.org/10.1080/00268948908065789

Mol. Cryst. Liq. Cryst., 1989, Vol. 171, pp. 103–116
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Printed in the United States of America

Studies of Organic Semiconductors for 40 Years—VII

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In Canada the systematic investigation of organic semiconductors started in the mid 1950's. This review of the contribution of Canadian scientist to the field of organic semiconductors will be limited to discussing semiconducting properties of organic materials like electrical conductivity, carrier transport, and photoconductivity. Substantial spectroscopic work on organic semiconductors has been performed including optical spectroscopy (absorption, reflectance, luminescence, Raman), NMR, and ESR. Here spectroscopic measurements will only be covered inasmuch as they illuminate semiconductive material properties. Significant work has also been reported on organic xerographic photoreceptors and photovoltaic solar cells. This work will be covered to the extent of contributing to our understanding of electrical properties and material parameters in organic semiconductors. In recent years electrical properties of polymers have also attracted significant attention. These developments, however, are outside the scope of this review which will be concerned only with crystalline and polycrystalline molecular solids.

Early research on organic semiconductors was basic in nature and not driven by any particular practical application. Anthracene and other polyacenes were the favorite model system studied for many years. In the late 1960's and early 1970's it became clear that efficient xerographic photoreceptors can be produced based on organic materials. This gave a new impetus for research in the field of semiconductive and particularly photoconductive properties of organic materials. New applications were not however based on traditionally studied polyacenes but used a number of new classes of molecules like phthalocyanines, squaraines, perylenes, etc. In electrophotographic applications organic photoconductors are utilized as polycrystalline thin films or as dispersions of microcrystalline particles in a suitable binder. The reason for this is twofold. First, many photoconductive organic materials belong to the class of organic pigments which are not soluble in common organic solvents and also decompose before melting. It is therefore very difficult and often impossible to make large single crystals of these materials. Second, in modern photoreceptors charge generation and transport functions are performed by two different layers and it was found that it is advantageous to have a very thin photogenerator layer. A practical way to obtain those layers is to cast thin films of submicron photoconductive particles in an appropriate binder polymer. Obviously the study of such "dirty" systems required development of new experimental techniques, some of which will be described later in this review.

In Canada, research on organic semiconductors has been pursued by several institutions including National Research Council in Ottawa and Xerox Research Centre of Canada in Mississauga, Ontario, established in the fall of 1974. In this review I will cover the work performed in these institutions. I will take a historical approach and describe developments more or less as they happened, but allowing departures from strictly chronological presentation for the sake of continuity in presenting different subjects.

The first organic semiconductor to be widely studied, anthracene also attracted attention of researchers at the National Research Council. In the initial work by Chynoweth and Schneider[1] in the mid 1950's, semiconductive and photoconductive properties of anthracene crystals were studied using DC dark and photoconductivity measurements on sandwich and surface cells with platinum contact electrodes. These investigations established that the majority carriers were positive holes and that dark and photoconductivity properties were strongly influenced by the presence of traps. In further investigations the influence of exposure to various gases on the electrical properties of anthracene was studied.[2,3,4] Four different types of behavior were found: (1) irreversible increase in photoconductivity (Cl_2 and NO_2); (2) reversible increase in photoconductivity (BF_3, HCl, SO_2, NO, O_2); (3) reversible decrease in photoconductivity [NH_3,$(CH_3)_3N$, $(C_2H_5)2O$, C_2H_5OH, H_2O, $(CH_3)CO$]; and (4) no effect on photoconductivity [CO_2, N_2, Ar, $(CH_3)_4C$]. Type (1) and (2) gases are electron acceptors, (3) are electron donors, and (4) are inert. Neutron bombardment of anthracene[5] lead to a dramatic decrease in photoconductivity. All these observations were interpreted by assuming that new trapping levels are introduced by the corresponding treatment of anthracene crystals.

The influence of oxygen and crystal purity on semiconductive properties of anthracene made it necessary to pay much more attention to sample preparation and the ambient conditions in which measurements are performed. In a carefully purified and grown single crystals Compton, Schneider and Waddington[6] found the importance of using proper metal evaporated or aquadag electrodes (coloidal carbon dispersion) as opposed to contact platinum electrodes. By using a guard ring electrode structure this work also clearly demonstrated the existence of both surface and bulk currents in anthracene crystals which exhibit distinctly different behaviors. In the follow-up paper Kommandeur and Schneider[7] studied bulk photoconductive properties of anthracene single crystals. They found that photoconductivity action spectra have antibatic character and explained this observation by increased recombination when carriers are absorbed near the surface of the crystal. Later work on anthracene sublimation flakes[8] which were about 1 μm thick showed some unusual behavior which could not be explained. Front illumination of surface cells lead to action spectra which had antibatic character, while back cell illumination lead to symbatic action spectra behavior. 9,10-dichloroanthracene was found to exhibit 2 to 3 orders of magnitude higher photoconductivity than anthracene,[9] which extended to light wavelengths longer than the absorption edge.[10] This was attributed to light induced excitation of charge from about 1.2 eV deep trapping levels.

Similarly, the observed photoconductivity in anthracene induced by the 694.3 nm Ruby laser line was also explained by light induced excitation of trapped charges.[11] An alternative explanation is charge carrier generation originating from the triplet state which has been demonstrated experimentally by Sharp and Schneider.[12]

In a series of three papers Kommandeur, Korinek and Schneider[13,14,15] studied photoconductivity in a number of single crystals and sublimation flakes of different organic compounds using DC measurements on surface cells with silver paste or aquadag electrodes. In naphthalene, stilbene, diphenyl, terphenyl, β-methylanthracene, anthracene, and pyrene they found small activation energies for photoconductivity of a few tenths of an electron volt which were concluded to be associated with the charge carrier transport process.[13] On melting, naphthalene and biphenyl showed a marked increase of both dark conduction and photoconductivity[14] which were associated with changes in carrier mobilities. This work also demonstrated that crystalline order was not a necessary condition for photoconductivity. Investigations of photoconductivity action spectra[15] showed that in pyrene three pronounced photoconductivity peaks are observed in the wavelength range 400 nm to 450 nm, where no optical absorption can be detected. Similarly naphthalene showed strong surface photoconductivity at long wavelengths (around 320 nm) where absorption is weak. Terphenyl and stilbene, also showed photoconduction at long wavelengths (as far as 800 nm) where optical absorption was very low. These observations were speculated to originate either from impurity states or intrinsic charge transfer states. In azulene photoconductivity was detected only from the second excited singlet state. Kokado, Hasegawa, and Schneider[16] studied semiconductive and photoconductive properties of perylene-fluoranil charge-transfer (CT) complex crystals grown from a toluene solution. They found anisotropic conductivity and photoconductive response extending to more than 1300 nm into the IR and also observed risetimes and fall times of photocurrents on the order of minutes. These results were interpreted as an extrinsic photogeneration process combined with strong carrier trapping.

The realization of the importance of traps in semiconductive and photoconductive properties of organic materials have stimulated the use of thermally stimulated currents (conductivity glow-curves) to determine trap energy levels. Measurements on anthracene[17] showed dominant trapping level at 0.8 eV and less pronounced levels at 0.6 eV and 0.7 eV. 9,10-dichloroanthracene[15] showed a distribution of levels centered at 0.8 eV. Later measurements on crystals grown from zone refined anthracene[18] showed a trap level with an energy of 0.76 ± 0.05 eV and general decrease in thermally stimulated current peaks and photoconductivity on deliberate doping of the crystal with tetracene, or anthraquinone, or 9,10-dimethylanthracene. These results were explained by impurity induced reduction of the carrier generation efficiency.

The first successful observation of recombination fluorescence of electrons and holes injected into the opposite sides of an anthracene single crystal was reported by Helfrich and Schneider.[20] The hole injecting electrode consisted of a saturated solution of anthracene and $AlCl_3$ in nitromethane and the electron injecting electrode was prepared by reacting sodium with a solution of anthracene in tetrahydrofuran. Upon applying a bias of few hundred volts they observed blue luminescence emanating from the 2 mm thick region near the positive electrode of a 5 mm thick crystal. For current densities in excess of 2×10^{-9} A/cm^2 the intensity of the emitted light was a linear function of the magnitude of the injected current. At lower current densities the light intensity was falling off more quickly. The estimate of cross section for electron-hole recombination confirmed that basically coulomb attraction is governing the recombination rate. Subsequent work on the transient behavior of injected space charge limited currents and recombination radiation[21] enabled more precise determination of the recombination rate constant. It was found to be in agreement with the theoretical model which predicts that the rate constant is also mobility dependent. The experiments also showed the existence of fast and slow components in recombination luminescence whose ratio was found to be $I_{slow}/I_{fast} = 0.65 \pm 0.1$. A beautiful argument[21] based on recombination statistics of carrier pairs to form singlet and triplet states and on statistics of triplet state annihilation predicted that this ratio should be equal to 0.6, which is in excellent agreement with the experimentally obtained value.

The studies of electron photoemission from anthracene crystals by Pott and Williams[22] showed that photoemission characteristics are strongly wavelength dependent. At long wavelengths (330–410 nm) singlet-singlet annihilation process was identified as a source of photoelectrons. For wavelength below 330 nm down to 260 nm CT-CT state annihilation or CT state carrier interactions have been identified as the source of photoelectrons. The studies of electron drift mobility in normal and deuterated anthracene along the c′ direction gave 75% probability that there is a positive deuterium effect on the mobility component studied.[23] Measurements of electron Hall mobilities in anthracene[24] did not reveal any anomalies theoretically predicted in materials with narrow bands.

The discovery of recombination fluorescence in anthracene supplied with liquid contact electrodes motivated the search for solid state ohmic contacts for this material. In two papers by Schadt and Williams[25] and Pott and Williams,[26] a method for preparation of hole injecting and electron injecting solid state ohmic contacts was described. Ohmic contact for holes was prepared starting with a saturated solution of $AlCl_3$ and anthracene in nithromethane. Upon drying of a drop of this solution on the surface of anthracene, an ohmic contact was formed which could sustain currents up to 10^{-4} A/cm^2. Similarly an ohmic contact for electrons was obtained when a concentrated solution of sodium and anthracene in tetrahydrofuran in contact with the anthracene crystal surface was evaporated until dryness. Electron ohmic contact showed the onset of saturation at currents as large as 10^{-2} A/cm^2. These contacts functioned also well at low temperatures at least down to 77°K, which enabled the studies of the space charge limited currents (SCL) as a function of temperature. These measurements enabled determination of the trapping levels for holes and electron mobilities by SCL current transients for different crystalographic directions. Holes were found to exhibit an exponential trap distribution with the total density of about 10^{16} cm^{-2}, together with two discrete levels at 0.53 eV with a density of 10^{15} cm^{-2}, and at 0.24 eV with a density of 10^{20} cm^{-2}. The values for trapping levels are similar to the previous determination using thermally stimulated currents.[17] The differences may be due to differences in the material itself or due to systematic errors inherent to the different experimental techniques employed. For electrons drift mobilities were measured using SCL current transients in the temperature range from 170°K to 300°K. Mobility along the a axes had a value of 1.5 cm^2/Vs at room temperature increasing to 2.3 at 170°K. Mobility along the b axes appeared basically constant and equal to 1 cm^2/Vs, while the mobility along the c' axes decreased from 0.4 at room temperature to about 0.25 at 170°K.

The developed solid state ohmic electrodes for anthracene were used to construct an electroluminescent diode.[27] Interestingly it was observed that in order to obtain electroluminescence it was important to have good electron injecting electrode. Any other positive electrode, including the one used for electron injection would inject holes and lead to electroluminescence. In the systematic study of pulsed and DC electroluminescence in anthracene equipped with solid state electron and hole injecting contacts Williams and Schadt[28,29] concluded that hole injection mechanisms for ohmic and nonohmic hole contacts must be different as they showed distinctly different transient electroluminescence characteristics. Nonohmic hole injecting contacts was concluded to be an exhaustion-type Schottky barrier, particularly under high fields. However, irrespective which hole injecting contact was used, electroluminescence was proportional to current over five orders of magnitude for temperatures between 128°K and 323°K. The electroluminescence spectrum was found to depend on the crystal growth procedure, which was interpreted by different amounts of produced fluorescing defects. The theoretical analysis of double injection experiments in anthracene satisfactorily produced the observed current-voltage characteristics.[30]

In recombination electroluminescence devices, large concentrations of free carriers and excitons are encountered in the recombination zone. These different species can interact and lead to new phenomena, which may be important for the performance characteristics of electroluminescent devices. These problems were addressed in a series of papers in which free carrier exciton interactions were investigated. Wakayama and Williams[31,32] studied the quenching of prompt and delayed fluorescence by injected electrons and holes. They found that triplet excitons are strongly quenched by carriers while singlet excitons are not. The quenching of delayed fluorescence, however, could not be explained by quenching of precursor triplet excitons alone but required postulating the existence of an intermediate state in the triplet to singlet fusion process which is strongly quenched by carriers. In these experiments excitons were generated optically and carriers were injected by using a carefully selected electrode pair which produces little or no electroluminescence. Similarly delayed electroluminescence was observed to be quenched by injected carriers.[33] In order to explain the details of the quenching process it was proposed that the intermediate state in the singlet to triplet fusion process is essentially a quartet state produced by interaction of a triplet state and a free carrier.[34] However, no independent confirmation for the existence of this state was obtained.

Electroluminescence in pentacene doped anthracene crystals was studied by Wakayama, Wakayama, and Williams.[35,36] They found two components in the spectral distribution of electroluminescence corresponding to anthracene intrinsic fluorescence and to pentacene fluorescence. In the time domain three components of electroluminescence decay after pulsed excitation were observed. The short component with lifetime shorter than 10 μs was assigned to direct singlet recombination. 2–3 ms lifetime was associated with triplet exciton annihilation, and the longest lifetime in the millisecond range was associated with trapped-detrapped carrier recombination. Optically excited fluorescence spectra showed only anthracene fluorescence, while electroluminescence showed a strong pentacene component. This indicates that pentacene is an efficient carrier but not energy trap. In general the quantum efficiency for electroluminescence was about 10%.

Carrier mobilities have been studied in anthraquinone,[37] biphenyl,[38] 9,10-dichloroanthracene,[39] and 1:1 complexes of tetracyanobenzene with naphthalene, anthracene, and durene.[40] For anthraquinone[37] holes were immobile and electron mobilities at room temperature have been found to be highly anisotropic having the values of 0.28, 0.20, and 0.022 cm^2/Vs for c′, b, and a crystallographic directions respectively. This observed anisotropy was contrary to predictions of some theoretical calculations. Traps about 0.2 eV deep at the concentration of about 200 ppm controlled mobility at low temperatures. In biphenyl[38] also only electrons were found to be mobile. Carrier generation induced by 337 nm nitrogen laser pulses depended on the third power of light intensity which was interpreted as an indication of photoionization of singlet excitons produced by two photon absorption. Room temperature electron mobility in this material was slightly anisotropic: 0.42, 1.25, and 0.51 cm^2/Vs for a, b, and c′ crystal directions, respectively. For a and c′ crystal directions mobilities were proportional to T^{-1} and for the b direction to $T^{-1.25}$ indicating that in biphenyl carrier transport is intermediate between adiabatic and nonadiabatic approximations. On the other hand in 9,10-dichloroanthracene only holes were found to be mobile.[39] At room temperature mobilities were found to be isotropic in the ac plane and equal to 0.6 cm^2/Vs. In the direction normal to this plane mobility was smaller amounting to 0.18 cm^2/Vs. At lower temperatures the mobilities were thermally activated indicating the existence of a trapping level at 0.25 eV. 1:1 complexes of tetracyanobenzene with naphthalene, anthracene, and durene all showed practically isotropic mobilities with values about 3 cm^2/Vs indicating that the free carriers are probably delocalized.[40]

DC and AC conductivities of vacuum evaporated thin films of tetrathiotetracene were studied by Webb and Williams.[41] The transport of free carriers was concluded to be controlled by potential wells associated with tetrathiotetracene-oxygen complexes which had a density of about 10^{19} cm^{-2}. DC conduction was described as hopping between different wells, while the fact that AC conduction was larger was attributed to additional charge motion within individual wells. A thermal activation energy for DC conduction of 0.28 eV was found to be in good agreement with a Poole-Frenkel analysis of high field data which gave a barrier height of 0.26 eV. In a subsequent paper studies of coevaporated thin films of tetrathiotetracene and o-chloranil were presented.[42] Significant conductivity enhancement was observed in both materials when the other material is present as a dopant in small quantities. The existence of doping effects was also confirmed by ESR measurements.

The phenazine crystals showed photoconductivity originating from both singlet and triplet absorption.[43] The carrier generation through singlet absorption appears to be an extrinsic process in which mobile electrons and trapped holes are produced. Photoconductivity produced by the triplet absorption appears to involve a hole detrapping process. In phenazine, unlike anthracene, carrier generation could not be explained by the Onsager theory of geminate recombination.[44] Pulsed laser techniques were used to study photoconductivity in anthracene, phenazine, iodoform, and tianthrene.[45] Measurements on anthracene were in agreement with previous results using dc photocurrents; in phenazine carrier generation was interpreted as two photon absorption yielding a singlet exciton which produces carriers; measurements on iodoform indicated a bulk generation process involving states other than the singlet, and in thianthrene 1.5 power dependence of dc photocurrents suggested that carrier generation is a result of singlet-triplet exciton interactions.

Photoconductivity studies in an anthracene-tetracyanobenzene charge transfer complex by pulsed laser excitation[46] showed that the photogeneration process involves thermal dissociation of the lowest lying charge-transfer state. General features of photogeneration were satisfactorily explained by a simple one dimensional kinetic model. In the same material the phenomenon of delayed fluorescence quenching by photogenerated carriers has been observed.[47] The explanation of the observed experimental data required postulating a long lived CT state. Photoconductivity in 1:1 thianthrene-tetracyanobenzene[48] was shown to be dominated by extrinsic processes, i.e. interaction of excitons with different types of defects. The results could be qualitatively interpreted in the framework of the one dimensional Onsager theory.

The discussion of the nature of electron phonon interactions (strong or weak vibronic coupling) in molecular crystals[49] was applied by Siebrand to anthracene, naphthalene, and pyrene.[50] For anthracene and naphthalene he proposed that vibronic interactions may be responsible for discrepancies between calculated velocities and measured mobilities in anthracene and naphthalene. For pyrene he concluded that carrier motion is more wavelike and should be therefore described by a band model. In the later work Munn and Siebrand developed a theory of charge transport in molecular solids for different limiting cases of coupling between charge carriers and phonons.[51–53] In the case that electronic exchange interactions are dominant there is coherent transport, while dominant electron-phonon interactions lead to hopping transport. They also assumed a quadratic interaction between charge carriers and molecular modes. They found that in anthracene, transport in different crystallographic directions can not be described by a single mechanism. In the c′ direction the values and temperature dependence of mobilities and the deuterium effect are well described by the slow electron hopping limit (narrow electron bands), which is characterized by a positive temperature coefficient of mobility, which is observed experimentally. All other mobility components for electrons and also measured hole mobilities show negative temperature coefficients and have been assigned to a slow-phonon coherent transport or a mode intermediate to hopping and coherent transport in the slow-phonon limit. (The slow-phonon limit implies that electron speed is limited by the slow speed of phonon motion.) The theory has been also applied to calculate Hall mobilities[54,55] and it predicted the possibility of sign anomaly. Comparison with experimental data for anthracene explained gross experimental features, but detailed comparison with experiment was hindered by conflicting reported results of the measurements. In the discussion of experimental results on anisotropic carrier mobilities in naphthalene Munn and Siebrand[56] concluded that for holes mobility in at least one direction can not be hopping in nature, while hopping mobility mechanism in all directions was consistent for electrons.

An interesting development in our understanding of the nature of geminate electron-hole pairs in anthracene and related aromatic hydrocarbons has been initiated by Bounds and Siebrand.[57,58] They calculated energies of charge transfer states in anthracene and argued that initial charge separation is a result of a charge transfer transition rather than autoionization of hot Frenkel exciton states. The calculations were later refined[59] and also applied to pentacene[60] with basically the same conclusions. For both materials they have shown that the charge transfer (CT) state energies can be, with reasonable accuracy, approximated with a Coulomb energy calculated using an average isotropic dielectric constant. Calculations provided qualitative agreement with activation energies and observed carrier yields as a function of wavelength. An approximate calculation of time evolution of the carrier generation process predicted a risetime on the order of 20–50 ps for the photogenerated current in anthracene.[61]

This attractive picture of the charge transfer exciton as a precursor for photogenerated carriers in anthracene and other polyacenes was found to give inconsistent charge transfer exciton radii deduced from photoconductivity and electroabsorption measurements.[62] Calculation of the spectroscopic assignment of charge transfer excitons in anthracene, tetracene, and pentacene gave qualitative agreement with the observed intensity distributions.[63] Further refinements of the theory showed that lowest lying CT transitions in anthracene are split by inter and intracell electron-hole transfer integrals leading to four rather than three bands in the 3.5 to 3.8 eV range,[64] the evidence for which was also found in the experimental spectral data. The resolution of inconsistency between CT exciton radii determined spectroscopically and from photoconductivity measurements was recently proposed by Siebrand, Ries, and Baessler.[65,66] They noticed the discrepancy between the band gap in anthracene determined spectroscopically (4.4 eV) and by photoconductivity measurements (4.1 eV) and assigned it to the lattice deformation energy of 0.18 eV per carrier in the nonrelaxed lattice after optical excitation. They then proposed that carrier generation proceeds via a nonrelaxed CT exciton having 1 to 1.5 nm radius which can lose the excess energy either by vibrational relaxation or by a single hop to a near neighbor in the crystal. This proposal is consistent with both optical CT exciton radii and CT exciton precursors to photogenerated carriers. It however requires the explanation of the large deformation energies which has not been theoretically justified at present.

Research on organic semiconductors in the industrial environment has been motivated mainly by potential applications in electrophotography. The materials of interest had therefore to be sensitive in the visible part of the spectrum. One class of such compounds are phthalocyanines which have been widely studied for their semiconductive and photoconductive properties. Pulsed photoconductivity measurements on evaporated thin films of β-metal-free phthalocyanine[67] have revealed that carrier generation is probably an extrinsic process connected with oxygen absorption. The interesting important feature of carrier generation efficiency (also referred to as quantum efficiency of carrier generation, carrier yield, or gain) in that material was the lack of wavelength dependence from the absorption edge in the red up to the near UV part of the spectrum. This observation immediately suggests that the precursor of photogenerated carriers is the first excited singlet state. If that is the case the study of fluorescence quenching as a function of the applied electric field should give information as to whether the first excited singlet state is a direct or indirect precursor of photogenerated carriers. For electric field dependent generation efficiency, which is usually the case in organic photoconductors, fluorescence quenching by the external electric field is expected if the excited singlet state is a direct carrier precursor. Indeed a strong fluorescence quenching by the electric field has been observed in the x-polymorph of metal free phthalocyanine by Menzel and Popovic[68] and the relative change of fluorescence agreed with the photogeneration efficiency measured xerographically. In subsequent work in addition to β and x polymorphs of metal-free phthalocyanines, a magenta pigment, 2-methoxy-5′-nitrophenylazo-2-naphthal-3-phenylcarboxamide (NRB), and a yellow pigment, 8,13-dioxodinaphtha[2,1,2′,3′]furan-6-(2″-pyridyl)-carboxamide (DFC), have also been investigated with respect to electric field induced fluorescence quenching.[69] Of all these only the yellow pigment DFC showed unexpected fluorescence enhancement with the increasing field, showing that some other mechanism than direct dissociation of the first excited singlet state lead to the photogenerated carriers in that material. It therefore appeared that strong fluorescence quenching by applied electric field is a signature of high quantum efficiency of carrier generation, but that there are other mechanisms leading to photogenerated carriers which do not lead to fluorescence quenching.

After Loutfy and Sharp[70] demonstrated the photovoltaic effect in Schottky barriers of x-metal-free phthalocyanine the photovoltaic cell structure has been used to investigate sensitization phenomena by surface doping of phthalocyanine microcrystalline particles.[71] Depending on the dopant used both sensitization and desensitization were observed and also the phenomenon of spectral sensitization in which the photovoltaic wavelength response was modified by absorption characteristics of the dye used for surface doping. Charge versus energy transfer mechanisms were considered to explain the observed behavior. It was concluded that sensitization is basically a charge transfer phenomenon. In the investigation of surface doping by electron donor and acceptor molecules[72] a marked correlation between increased carrier yield and fluorescence quenching induced by doping was observed. This was attributed to the migration of the singlet excitons to the surface and subsequent quenching by charge transfer and exciplex formation. Experiments involving deliberate doping of x-metal-free phthalocyanine by other metal phthalocyanines[73] showed that most metal Pc's increased carrier generation efficiency in photovoltaic cells indicating the existence of an extrinsic process for carrier generation. The theory of transition metal doping of metal free phthalocyanine was developed by Loutfy and Cheng[74] and applied to explain the correlation between semiconductive and photoconductive properties and trap density in different polymorphs of metal free phthalocyanine.[75]

Deep trapping and slow impurity ionization dynamics have required development of some special experimental tools for studies of metal-free phthalocyanine photovoltaic cells. It was found that measurements of integral, as opposed to differential junction capacitance is advantageous in determining barrier properties.[76] Alternatively special low frequency methods can be used.[77] The density and energy levels of traps governing charge transport in x-metal-free phthalocyanine Schottky barrier photovoltaic cells were studied by measuring cell properties as a function of temperature and applied bias and using space charge limited current theory to interpret the results.[78-80] The studies of the mechanism of photogeneration in this system by pulsed[81,82] and DC[83] excitation techniques revealed that carrier generation is a local phenomenon occurring efficiently only in the space charge region of the barrier. Moreover, for reversed biased cells the carrier generation efficiency approaching unity was observed, which could not be explained on the basis of the average electric field in the barrier and carrier yields measured xerographically. This lead to the proposal of the model in which the carrier generation is dominated by the strong electric field around ionized impurities which act as charge generation centers by dissociating excitons which diffuse into their vicinity.[84] The major features of this model were supported by the results of pulsed photoconductivity measurements as a function of temperature.[84]

Electroluminescence properties of x-metal-free phthalocyanines microcrystals have been studied by Code and Popovic.[85] The electroluminescence in the pigment dispersed in the polymer matrix was induced electro-optically. The sample was first illuminated by strongly absorbed light in the presence of an external electric field. Photogenerated and separated electrons and holes were then allowed to recombine by shorting the cell electrodes which resulted in the burst of recombination fluorescence. Field dependence of the recombination fluorescence was consistent with the Poole-Frenkel model, and the temperature dependence of the fluorescence signal showed an activation energy of 0.16 eV which was interpreted as the depth of the traps filled by carriers in the photoinduced generation step.

A theory of measurements of carrier generation efficiencies in photoconductive particle dispersions in inert polymer matrixes was developed by Popovic.[86] The analysis has shown that the conventional formula for the quantum yield, valid for a homogeneous sample, has only to be multiplied by a factor which is roughly equal to the volume fraction of the photoconductive pigment in the particle dispersion. Measurements on x-metal-free phthalocyanine dispersions gave results consistent with previous xerographic measurements. Due to uncertainties of the geometric shapes this method has an intrinsic error of about 20%.

In a series of papers a quantitative correlation between the electric field induced fluorescence quenching was studied in the x[87,88] and β[89,90] polymorphs of metal free phthalocyanine. In these experiments photoinduced electrical response to pulsed laser illumination was measured simultaneously with the sample fluorescence. In order to minimize the influence of carrier trapping a delayed collection field technique was utilized for photoresponse measurements. The results showed that the electric field induced fluorescence quenching and photoinduced carrier generation are indeed different expressions of the same phenomenon which is dissociation of the first excited singlet state into carriers. When transformed in a proper fashion fluorescence quenching and carrier generation were shown to exhibit the same temperature dependence.[87] They were found to be linearly correlated at higher fields, with departures from linearity observed at low fields. This was explained by proposing that the carrier generation is a two step process involving the creation of an intermediate charge transfer state.[88] At high fields this state dissociates with unit efficiency to form free carriers. At lower fields some of the charge transfer states recombine thus decreasing the number of photogenerated carriers. In both materials it was observed that the geminate electron-hole pairs live for a long time and show nonexponential decay kinetics on an unexpectedly long time scale extending to tens of milliseconds. This is probably caused by the interaction of charge carriers and trapping sites. The attempts to fit fluorescence quenching and carrier generation data to the theory developed by Noolandi and Hong[91] lead to fits which were not satisfactory at low electric fields.[88] In the β polymorph low field data could be satisfactorily interpreted in the framework of the Poole-Frenkel model.[90]

In the work described in the previous paragraph correlation was found between fluorescence quenching and relative photoresponse, as determination of absolute carrier generation efficiencies for particle dispersions has an intrinsic uncertainty as mentioned before. In work on chloroindium phthalocyanine[92] an evaporated thin film of the pigment was overcoated with the hole transport layer allowing charge separation across the whole cell thickness and accurate determination of quantum efficiency. Excellent quantitative correlation was found between carrier generation and fluorescence quenching and it was concluded that in that material carrier generation is a bulk, rather than a surface pigment property.

The applications of different metallophthalocyanines as photogenerator materials in organic solar cells[93] and xerographic photoreceptors[94–97] has been discussed by Loutfy and coworkers. This work described solvent induced dimorphic changes leading to the appearance of new absorption peaks in the near-IR part of the spectrum (around 800 nm) and strong IR photoconductivity. The changes in absorption and photoconductive behavior have been attributed to solvent induced aggregation of phthalocyanine molecules.

Another class of highly efficient organic photoconductors are squaraine compounds. They are also of particular interest because many materials belonging to that class show strong photoconductive response in the near IR part of the spectrum. The investigation of DC photoconductivity, photovoltaic effect,[97] and xerographic properties[98,99] of dispersions of particles belonging to this class of compounds revealed that optical, electrical and photoelectrical properties of these materials depend strongly on the chemical structure and morphology of the dyes. At low fields carrier generation efficiency (gain) was found to be proportional to the square of the applied electric field. Some of the most sensitive compounds were found to be OH, CH_3, and H anilinosquaraines, with extrapolated quantum efficiency for carrier generation of 0.7, 0.5, and 0.1, respectively, at the field of 100 V/μm.

Photoconductivity in perylene tetracarboxyl-diimides was studies by Popovic, Loutfy and Hor,[100] using pulsed photoconductivity and electric field induced fluorescence quenching measurements. The results were in complete qualitative agreement with analogous experiments performed on phthalocyanines, supporting the carrier generation mechanism originating from the first excited singlet state and proceeding via an intermediate charge transfer state. However, the studies of both phthalocyanines and perylenes could not confirm dissociation of a free singlet exciton into carriers, as the measured integrated fluorescence intensity could originate from trapped excitons. In order to investigate whether free excitons can produce carriers a study of time resolved fluorescence quenching in bis(methyl)perylene tetracarboxyl diimide was undertaken.[101] The results convincingly showed that free excitons are participating in the carrier generation process, but the photoconductivity component originating from trapped excitons was also detected. An interesting charge generation mechanism was uncovered in thin films of a perylene pigment overcoated with a hole transport layer comprised of tetraphenyldiamine charge transport molecule dispersed in a polycarbonate matrix.[102] The carrier generation mechanism in this system was demonstrated to be of the sensitized type. It involves the diffusion of the photogenerated exciton to the interface of the dye and hole transport layer, where it dissociates producing an excess electron in the dye and a hole in the transport layer.

In the last decade the emphasis in organic semiconductor research has shifted from studies of polyacenes to materials used in electrophotography. Some important advances have been made in understanding photoconductivity mechanisms in these materials, but we are still far from having a full and consistent picture. Organic semiconductors, with the infinite versatility of carbon chemistry, will remain an exciting field of research for years to come.

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