Spectroscopic Study of Charge Transfer Complexes of Organic and Metal-Organic Photoconductors

A Thesis Submitted

By

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This thesis is on spectroscopic study of charge transfer complexes (CTCs) of organic and metal-organic photoconductors containing study of FTIR spectra of CTCs of some organic photoconductors and CTCs of metal phthalocyanine. Organic photoconductors are known from a long time but applications in opto-electronic devices are being studied only recently. These applications include opto-electronic devices like MOSFET, Phototransistors, photodiodes, photovoltaic devices, organic LEDs etc. Metal chelates of phthalocyanine (PC) legand such as CuPC, CoPC, NiPC, ZnPC, MgPC, PbPC and FePC have become famous in this regard. They also find applications as gas sensors. Most of them are low-dimensional conductors having highly anisotropic structural, electronic and optical properties because of metal chains in one crystallographic direction. Very less work is reported on CTCs of metal chelates with organic acceptors. This has been attempted in the present work. The phenomenon of photoconductivity is related with life-time of charge carriers determined by formation and recombination of electron-hole pairs and trap-limited conduction. Other important factor in photoconductivity is signal-to-noise ratio. There is generation of noise in almost all photoconductors. Noise is also observed in IV-VIS-near IR and FTIR spectra of light absorption in many photoconductors. Recently we studied spectroscopy of CTCs of organic photoconductors such as biphenyl, indigo carmine, β-carotene, green malachite, aniline blue, crystal violet and quinhydrone. We found scattering of charge carriers by light particles, spin-orbit split valence band interband transitions, noise in absorption spectra as well as Gaussian envelopes associated with electronic delocalization.

In the present thesis we have studied some more CTCs of organic photoconductors such as Acridine Orange (AO), Pinacyanol Chloride (PC), Rose Bengal (RB), Phenosafranin (Ph) and Methyl Violet (MV). Apart from these CTCs of eight metal phthalocyanines such as CuPC, NiPC, CoPC, ZnPC, PbPC and SnPCO which are photo conducting are undertaken for their spectroscopic study. FePC and MnPC which are magnetic and not showing any photoconductivity are also studied for a comparative study.

1. GENERAL CONCLUSION:

The first part of the thesis deals with charge transfer complexes of organic photoconductors such as Acridine Orange, Pinacyanol Chloride, Phenosafranine, Rose Bengal and Methyl Violet. The FTIR spectra were studied with showed noise in absorption as it should be in photo-conducting materials. Oscillations in the density of states were found. Acridine orange complexes showed two or more absorption edges. Pinacyanol did not behave as a macromolecule as found from the spectra. The CTCs of Pinacyanol Chloride (PC), the band gap was reduced by 0.04 eV from 0.25 eV. Imperfect nesting was found in CTCs of PC. Triangular distribution might be related with internal Frenz-Keldysh effect. The CTCs of phenosafranine showed asymmetric Gaussian bands in FTIR spectra. Two absorption edges were found. Exciton-phonon coupling was found in the Chloranil complex. Full Width Half Maximum (FWHM) was different in both sides of a Guassian band. Rose Bengal behaved as an inhomogeneous and plastic material. Hopping transport was indicated by half power beta density. Precursors of a signal in dispersive medium were described by Airy functions and more generalized function. Rose Bengal and its CTCs were non-linear optical media. Methyl violet is also known as a triphenyl methane dye. Methyl violet also formed semiconducting CTCs with organic acceptors. Band assignments are similar to CTCs of crystal violet. Spin-orbit split valence band was concluded on the basis of these transitions from valence sub-bands to a conduction band. Square-power beta densities revealed hopping transport in ionic solids.

The second part of the present thesis dealt with CTCs of metal phthalocyanines of eight different metals. ZnPC, PbPC and SnPCO were highly photoconducting and the FTIR spectra showed a range of free-carrier absorption. Most of them were two-dimensional conductors as observed with nature of transition. Gaussian bands were also found which were associated with electronic delocalization oscillations in the density of states with square-root singularities in one dimension were also found. There are photoconducting domains in these two dimensional photoconductors. CuPC, NiPC and CoPC were taken as moderately photoconducting and partially anti-ferromagnetic materials.

There is a competition between photon-donating domains and magnetic domains as found in type II superconductors. FePC and MnPC were found to be non-photoconducting and ferro-magnetic materials. The FTIR spectra showed non-degenerate semiconducting behavior. Here the photocurrents cancel each other to give almost zero photocurrents.

2. FUTURE SCOPE OF WORK

There is a lot of work to be done in the field of organic and metal-organic photoconductors. The effect of charge transfer in photoconducting materials can be studied directly by studying photo-currents and I-V characteristics of CTCs studied here. Temperature dependence of photocurrents can provide information about photoconducting band gap in these intrinsic photoconductors. The detail of photoconducting domains can be extracted through a study of fast and sluggish response of photoconductors and study of life-times of charge carriers. Even the temperature dependence of life time can be studied. Photoconducting current distribution and current saturation can be studied. Optical probing of acoustic flux associated with moving domains can be carried out. Transient approach to current saturation also can be studied. Current oscillations and high field domains can be investigated.

3. APPLICATIONS

Organic and metal-organic photoconductors can be used in mainly opto-electronic devices such as photo-diodes, phototransistors, photovoltaic devices, photoelectric materials, photo-detectors and solar cells. There will be large photocurrents even at low temperatures due to small band gap compared to inorganic or elemental photoconductors. The efficiency of a solar cell increases at low temperatures. The effect of charge transfer is to increase dark current as well as photoconductivity. The CTCs are expected to be more photoconducting then organic and metal-organic photoconductors. The photo-effective materials can also be used in molecular electronics. Some of them can act as molecular multivibrators. Electronic devices such as unijunction transistors, rectifiers, filters, thyristors, FETs, thermistors, etc. can also be constructed out of organic and metal-organic photoconductors and their static and dynamic characteristics can be studied. Apart from these applications, even Zener diodes, field-effect transistors, light-emitting diodes, tunnel diodes etc. can be prepared. Metal phthalocyanines are sensitive to neutral and ionic gases and are therefore used as gas sensors. FePC and MnPC being ferromagnetic can be used wherever ferrites and garnets are used in magnetic and non-reciprocal devices. Faraday devices even can be prepared. They also can be used as shielding materials.