CHAPTER 4

VIBRATIONAL SPECTRA OF TERNARY ORGANIC CONDUCTORS USING DPPD
4.1 Introduction

Although there is a wide research on bimolecular charge transfer complexes [1-3] there are only a few reports on semiconducting or metallic (highly conducting) ternary CT complexes [4-7]. We have only recently focused on the ternary complexes [8,9] after studying many binary systems [10-12].

In the present study we consider ternary systems based on DPPD (N,N'-diphenyl-p-phenyllenediamine) as an organic donor with iodine as a common acceptor and varying organic acceptors such as chloranil, DDQ, TCNQ and TCNE. The ternary systems can have special physical properties like two band transport [13], impurity or associated band edges in band structure [14], commensurate-to-incommensurate transition [15], neutral-to-ionic transition [16], electron-exciton interaction [17], modified band tailing and alloying effects due to more disorder [18], etc. For the modifications of these characters of the binary systems which are semiconducting, we carry out spectroscopic study of the systems based on DPPD as organic donor.

DPPD (N,N'-diphenyl-p-phenyllenediamine) exists as a gray powder and forms blue or black or dark green charge transfer complexes with organic acceptors. (DPPD)$_5$I$_{12}$ is a famous CT complex which contain most resonating polyiodine chains [19,20].

4.2 EXPERIMENTAL DETAILS:

Here, DPPD was used to prepare ternary organic conductors such as DPPD-chloranil-I$_2$, DPPD-DDQ-I$_2$ DPPD-TCNQ-I$_2$ and DPPD-TCNE-I$_2$ where DDQ=2,3-dichloro-5,6-dicyano-p-benzoquinone, TCNQ=7,7,8,8-tetracyano-p-quinodimethane and TCNE= N, N, N',N'-tetracyanoethylene. The organic acceptors were grinded
with DPPD in a mortar till it formed dark blue or black CT complex also along with iodine-all in 1:1:1 molecular weight proportions.

Almost transmitting pellets of the above ternary CT complexes were prepared using a compressor and die with dry KBr (spectrograde) powder. The Perkin-Elmer spectrophotometer was used for taking the spectra in the mid-IR range, i.e. between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\).

4.3 Results and Discussion:

The infrared spectra of DPPD-chloranil-I\(_2\), DPPD-DDQ-I\(_2\), DPPD-TCNQ-I\(_2\) and DPPD-TCNE-I\(_2\) in the full range are shown in [Figure 4.1(a-d)]. There is no absorption envelope around nearly 1500 cm\(^{-1}\) except in the DDQ and TCNE complexes as found in the binary CT complexes [21,22]. The other ternary complexes based on benzidine and TMPD(N,N,N', N'-tetramethyl-p-phenylenediamine) also have not shown such envelopes. Rather, there are two absorption edges corresponding to two forbidden energy gaps between one valence and two conduction bands. The intermolecular distances are expected to be larger than the binary subsystems leading to less electronic conduction. In spite of this, the minimum energy required for free charge carriers is expected to decrease because of the penetration of the impurity band or associated band edge of the additional sub lattice within the semi conducting gap of a binary system. Two acceptors can lead to a nature similar to complex salts rather than simple salts. Complex salts are more conducting than simple salts because of segregated or sandwich structures in the place of alternative dative structures. This seems to happen in DDQ and TCNE complexes in which cases the electronic absorption envelopes are found near 1550
cm$^{-1}$. In these ternary systems, DPPD is almost doubly ionized for which the second ionization potential is low compared to benzidine and TMPD. The asymmetric and aliphatic nature of DDQ and TCNE, respectively also plays role which polarize easily as compared to symmetric and aromatic TCNQ and chloranil. Thus polar optical phonons lead to the formation of absorption envelopes associated with electron-intramolecular vibration coupling, similar to those found in binary complexes of tetramethylbenzidine [23].

The nature of transition is analyzed by plotting all the possible absorption functions for polycrystalline and amorphous materials against the photon energy [24]. The comparisons showed that the transition corresponding to the band gap of about 0.225 eV was direct band-to-band transition and also revealed to these low-dimensional organic conductors which is shown in [Figure 4.2(a-d)]. The band gaps of DDQ and TCNQ complexes were lowered by about 0.05 eV compared to chloranil and TCNE complexes which is of order of magnitude of phonon energy. The former cases showing forbidden direct transitions and the later ones showing allowed direct transitions owing to larger intermolecular distances forbidding the transition.
Figure 4.1 Infrared spectra of
(a) DPPD-chloranil-I₂
(b) DPPD-DDQ-I₂
Figure 4.1 Infrared spectra of
(c) DPPD-TCNQ-I\textsubscript{2} and
(d) DPPD-TCNE-I\textsubscript{2}
The lower infrared absorption edges shown in [Figure 4.3(a -d)] indicated always an indirect transition because of the additional conduction band appearing as an associated band edge which is likely to be shifted in the momentum in the band structure.

The last analysis carried out in the range below 800 cm\(^{-1}\) was about the momentum of scattering of free charge carriers. This analysis is above the pinning gap (E\(_g\)) for the charge density waves. The scattering analyzed by plotting log\(\alpha\) vs log \(\lambda\) was always (in all the four complexes) found to be due to acoustic phonons. This reveals the low-pass filter behaviour of the sound waves coupled with electronic motions. The waves of low frequency have larger group velocity than the high frequency waves [25]. In the TMPD and benzidine-complexes, the localization due to optical phonon coupling in this range was found. These lattice modes do not propagate beyond the unit cell.
Figure 4.2  Nature of transition in
(a) DPPD-chloranil-I₂
(b) DPPD-DDQ-I₂
(c) DPPD-TCNQ-I₂ and
(d) DPPD-TCNE-I₂

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Figure 4.3 Lower infrared absorption edges in
(a) DPPD-chloranil-I₂
(b) DPPD-DDQ-I₂
(c) DPPD-TCNQ-I₂ and
(d) DPPD-TCNE-I₂
**Figure 4.4** Free-carrier absorption $\hbar \nu > \hbar \nu_p$ for
(a) DPPD-chloranil-$I_2$
(b) DPPD-DDQ-$I_2$
(c) DPPD-TCNQ-$I_2$ and
(d) DPPD-TCNE-$I_2$
where $\nu_p$ is the pinning frequency
4.4 Conclusion:

The ternary complexes DPPD-chloranil-I$_2$, DPPD-DDQ-I$_2$, DPPD-TCNQ-I$_2$ and DPPD-TCNE-I$_2$ were found to be small band gap semiconductors and the effective band gap of 0.225 eV was reduced to 0.11 eV by the insertion of a band associated with additional sub lattice.
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