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Vibrational spectra of ternary organic conductors using DPPD

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Abstract

The ternary charge transfer complexes of the well-known organic donor namely diphenyl-p-phenylenediamine (DPPD) have been studied with FTIR spectroscopy. There are two absorption edges – one at the Peierls gap (0.225 eV) and the other at the half of it, i.e. at 0.1125 eV. There is non-universal additional shrinkage of the second gap due to electron-electron scattering. The third gap at 0.056 eV is not observed as observed in the case of benzidine ternary complexes. Rather a free-carrier absorption revealing scattering of charge carriers by acoustic phonons is observed in 700-1000 cm^{-1} range. This also shows that bipolarons are the charge carriers in DPPD ternary complexes.

Keywords: FTIR spectra, ternary complexes, additional shrinkage, bipolaron

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-phenylenediamine) 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 ternary systems based on DPPD as organic donor.

DPPD (N,N'-diphenyl-p-phenylenediamine) exists as a gray powder and forms blue or black or dark green charge transfer complexes with organic acceptors. (DPPD)₅I₁₂ is a famous CT complex which contain most resonating polyiodine chains [19, 20].

2. Experimental details

Here, DPPD was used to prepare ternary organic conductors such as DPPD-chloranil-I₂, DPPD-DDQ-I₂, DPPD-TCNQ-I₂ and DPPD-TCNE-I₂ 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} .

3. Results and Discussion

The infrared spectra of DPPD-chloranil-I₂, DPPD-DDQ-I₂, DPPD-TCNQ-I₂ and DPPD-TCNE-I₂ in the full range are shown in [Figure 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

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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 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.

The lower infrared absorption edges shown in [Figure 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. There is additional shrinkage of the indirect band gap at 0.1125 eV due to electron-electron scattering which is a two-particle (electron and hole both as charge carriers) gap.

The last analysis carried out in the range below 1000 cm^{-1} was about the absorption by 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 [Figure 4 (a-d)]. 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.

The free-carrier absorption found in $700\text{-}1000\text{ cm}^{-1}$ range shows that bipolarons (or biexcitons) are the charge carriers in DPPD ternary complexes. There is no bipolaronic or biexcitonic localization as found in benzidine complexes by

observation of a four-particle gap at 0.056 eV ($E_p/4$ –where E_p is the Peierls gap).

The conduction band valleys are shown [Fig. 4.5 (a-c)] in benzidine, TMPD and DPPD complexes. In benzidine complexes corresponding to E_p (Peierls gap of 0.225 eV), two-particle (electron and hole) gap $E_p/2$ and four-particle (two electrons and two holes) gap at $E_p/4$ or excitonic bipolarons are all found. In TMPD complexes, there is Burstein-Moss shift of Peierls gap in two complexes. However in the present DPPD complexes two band gaps – one at Peierls gap (of 0.225 eV) and another of two-particle ($E_p/2$) gap are found. The band at $E_p/4$ is not found. So bipolarons move freely in DPPD complexes. In the DPPD complexes, there is non-universal additional shrinkage of the lower band gap at 0.1125 eV .

Table 1: Band gaps and additional shrinkages in ternary CTCs of DPPD

Complex	Nature of transition	Band gap (eV)	Additional shrinkages (Δ_0 or Δ_1) (meV)
DPPD-DDQ- I_2	Forbidden direct	0.220	$\Delta_0=5$
DPPD-TCNQ- I_2	Forbidden direct	0.212	$\Delta_0=13$
DPPD-Chloranil- I_2	Allowed indirect	0.108	$\Delta_1=4.5$
DPPD-DDQ- I_2	Allowed indirect	0.10.5	$\Delta_1=7.5$
DPPD-TCNQ- I_2	Forbidden indirect	0.102	$\Delta_1=10.5$
DPPD-TCNE- I_2	Allowed indirect	0.112	$\Delta_1=0.5$

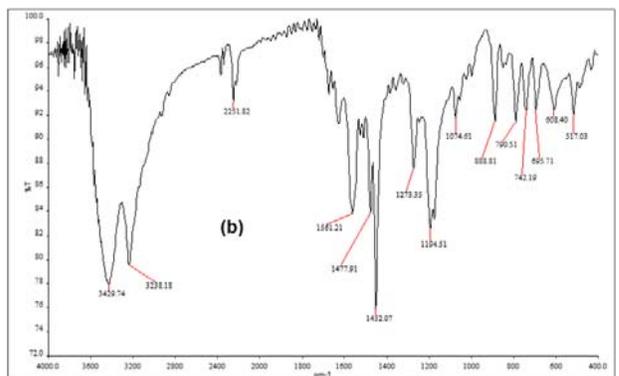
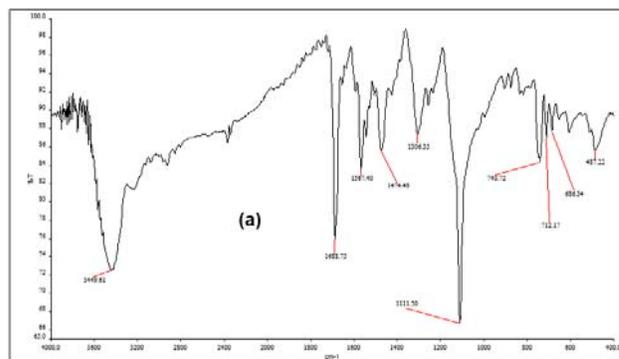


Fig 1: Infrared spectra of (a) DPPD-chloranil- I_2 DPPD-DDQ- I_2

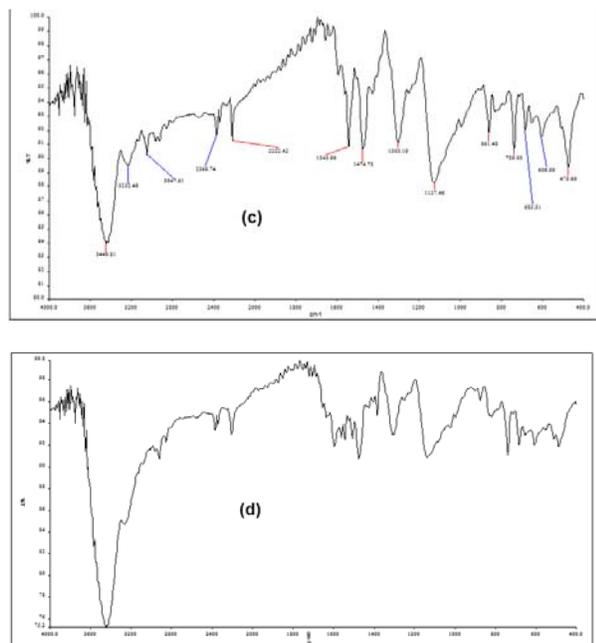


Fig 1: Infrared spectra of (b) DPPD-TCNQ-I₂ and (c) DPPD-TCNE-I₂

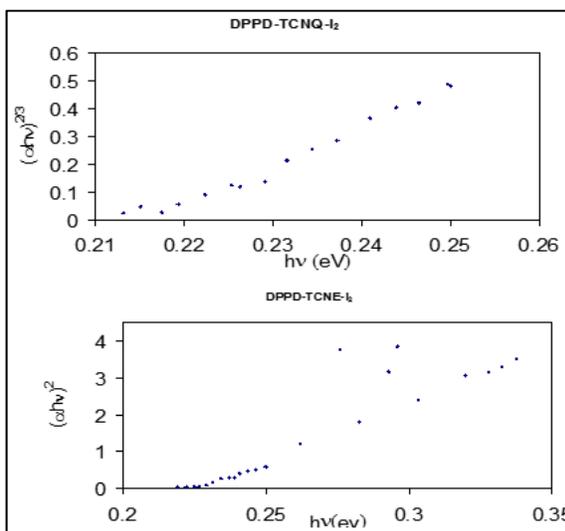
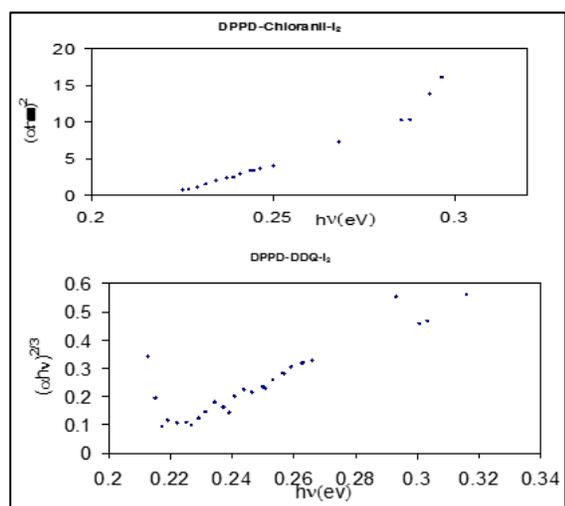


Fig 2: Nature of transition in (a) DPPD-chloranil-I₂ (b) DPPD-DDQ-I₂ (c) DPPD-TCNQ-I₂ and (d) DPPD-TCNE-I₂

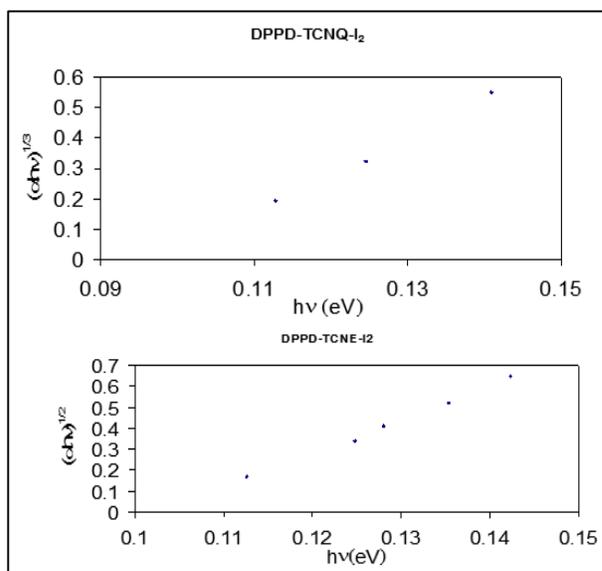
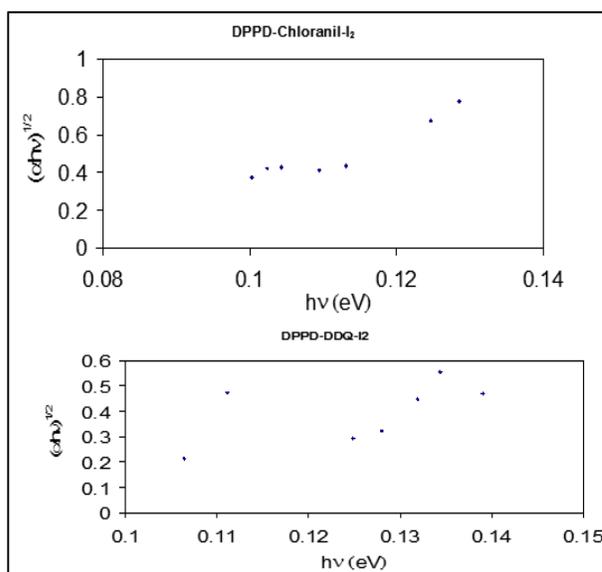
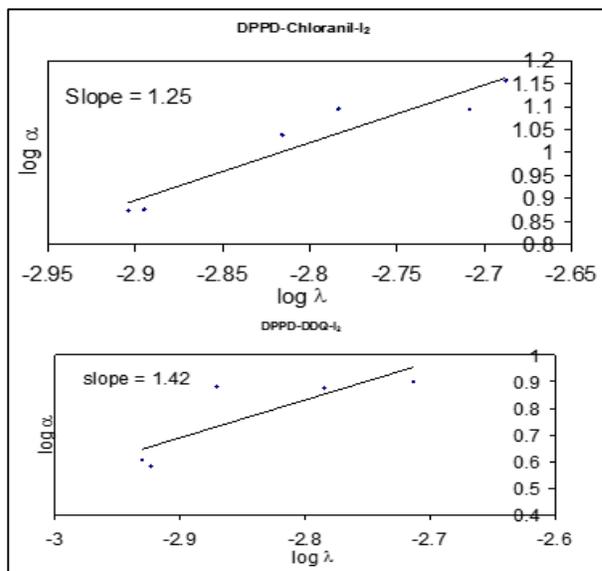


Fig 3: Lower infrared absorption edges in (a) DPPD-chloranil-I₂ (b) DPPD-DDQ-I₂ (c) DPPD-TCNQ-I₂ and (d) DPPD-TCNE-I₂



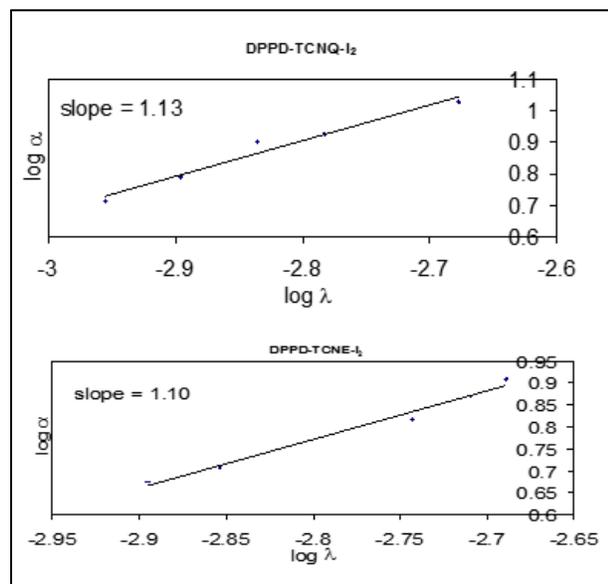
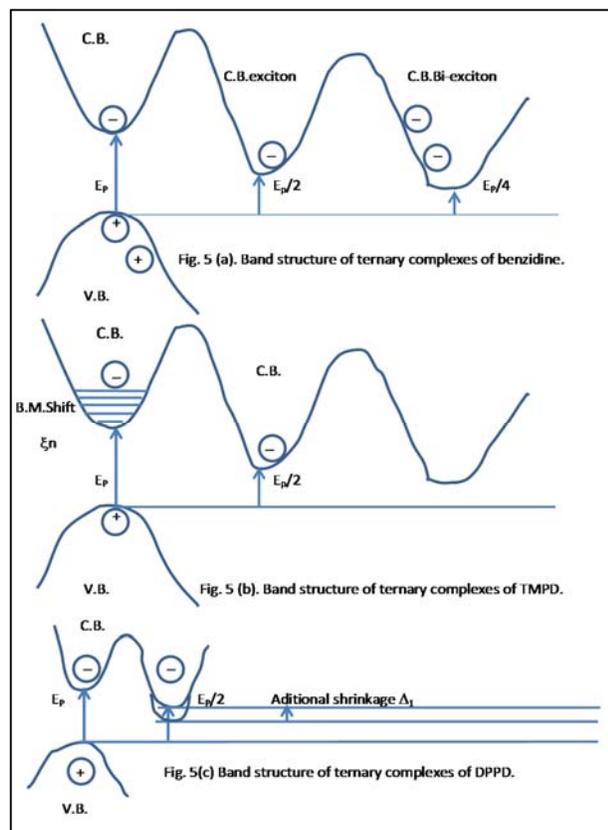


Fig 4:Free-carrier absorption $h\nu > h\nu_p$ for (a) DPPD-chloranil-I₂ (b) DPPD-DDQ-I₂ (c) DPPD-TCNQ-I₂ and (d) DPPD-TCNE-I₂ where ν_p is the pinning frequency



4. Conclusion

The ternary complexes DPPD-chloranil-I₂, DPPD-DDQ-I₂, DPPD-TCNQ-I₂ and DPPD-TCNE-I₂ 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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