



RESEARCH ARTICLE

INFRARED SPECTRA OF TERNARY CTCs OF TMPD

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ABSTRACT

The ternary charge transfer complexes of TMPD (N,N,N',N'- tetramethyl-p- phenylene diamine) have been studied with FTIR spectroscopy. The complexes have two-lower and higher-absorption edges in infrared range associated with two acceptors. TMPD-chloranil – I₂ have 0.22 eV and 0.12 eV as edges while TMPD-DDQ-I₂ have 0.28eV and 0.12 eV as edges. Similar edges at 0.22 eV and 0.09eV are found in TMPD-TCNQ-I₂ and 0.27 eV and 0.12 eV in TMPD-TCNE-I₂ complex. The analysis of free-carrier absorption shows scattering by acoustic phonons in TMPD-Chloranil-I₂ and TMPD-TCNE-I₂ complexes while impurity scattering in TMPD-DDQ-I₂ and TMPD-TCNQ-I₂ complexes. Chloranil and TCNE based ternary complexes are highly conducting.

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INTRODUCTION

Recently we have taken up the study of ternary charge transfer complexes based on standard organic donors and acceptors (Ashok N. Patel *et al.*, 2006). This study was inspired by the observation of superconductivity in the metal-ion based ternary complexes (Harrison *et al.*, 2001; Kini *et al.*, 1990). A comparison between binary and ternary complexes is required for understanding the modification in band structure in the ternary systems. In one donor-two acceptor systems, there is a possibility of two conduction bands associated with two acceptors. (William Paul in High Pressure, 1963; Katon and Mazcel Dekker, 1968). The complex may behave as a complex (1:2 or 2:3) salts rather than simple (1:1) salts. But there is a difference between a 1:2 complex salts and the ternary complex. The former having only one acceptor and the later having two different acceptors. The band structure will be modified due to two different electron affinities of acceptors in a ternary complex. The molecular structures of TMPD (N,N,N',N'-tetramethyl-p-phenylenediamine) and organic acceptors are shown in Figure 1. TMPD forms many interesting and well-known CT complexes (Oza, 1989). TMPD-chloranil is the complex studied rigorously as an organic semiconductor (7).

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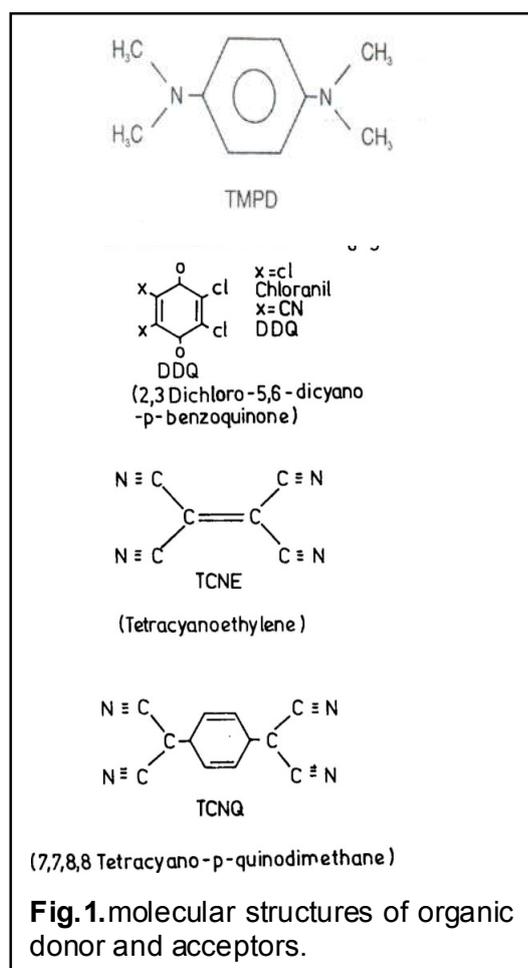
MATERIALS AND METHODS

TMPD was obtained as a white powder from Sigma chemical company, USA. It formed almost blue CT complexes with organic acceptors. TCNQ (7,7,8,8-tetracyano-p-quinodimethane), TCNE (tetracyanoethylene), DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) and chloranil obtained similarly were ground with TMPD and iodine in 1:1:1 molecular weight proportions in a mortar till the characteristic colours of CT complexes were obtained. The 5% CT complex was mixed with 95% KBr (spectrograde and dry) powder and reground till the complex dispersed homogeneously. The semitransparent mixture was pressed in a die by a manually operated compressor machine to form circular discs of regular size and shape. These compactations were used as samples by placing the specimens in a dark chamber of FTIR spectrophotometer of Perkin-Elmer Co., USA. The FTIR spectra were recorded in the full IR range between 400 cm⁻¹ and 4000cm⁻¹.

RESULTS AND DISCUSSION

TMPD has a lower ionization potential and is a smaller molecule as compared to benzidine. The interaction of TMPD with iodine as well as organic acceptors is stronger than that of benzidine. Thus CT complexes are strongly bound. The spectra of TMPD-chloranil-I₂ and TMPD-DDQ are shown (Figure 2).

The competitive binding of chloranil and iodine with TMPD molecule keeps neither chloranil nor iodine getting attached to TMPD which keeps TMPD in the neutral form.



Thus the spectrum of the ternary charge transfer complex contains bands of only (TMPD)⁰, which is neutral. However, in DDQ-Complex, there is semiquinone ion of DDQ molecule and TMPD becomes a dication TMPD²⁺ having development of four bands at 3222 cm⁻¹, 2638 cm⁻¹, 2429 cm⁻¹ and 2252 cm⁻¹. The ionic nature is also revealed by Lorentzian rather than Gaussian around 1100 cm⁻¹ in the mid-IR range. It is also supported by square-power beta density below 700 cm⁻¹. Both spectra show two transitions NT-1 and NT-2 in higher and mid infrared range. NT-1 is more clearly marked than NT-2 indicating stabilization of the normal conduction band as in a binary complex. Conduction band involving NT-2 is only partially stabilized. This range between 0.12eV and 0.18eV can be also alternatively viewed as electronic absorption envelope-an asymmetric Gaussian in the chloranil complex and a Lorentzian envelope DDQ complex. Thus DDQ complex is more like a non-degenerate semiconductor obeying a Lorentz model and chloranil complex obey degenerate semiconductor theory (8). The upper interband transition is an allowed direct transition obeying $\alpha h\nu = A(h\nu - E_g)^{1/2}$ with E_g=0.22eV for chloranil complex and E_g=0.28eV for DDQ complex (Figure 3(a) and 4(a)).

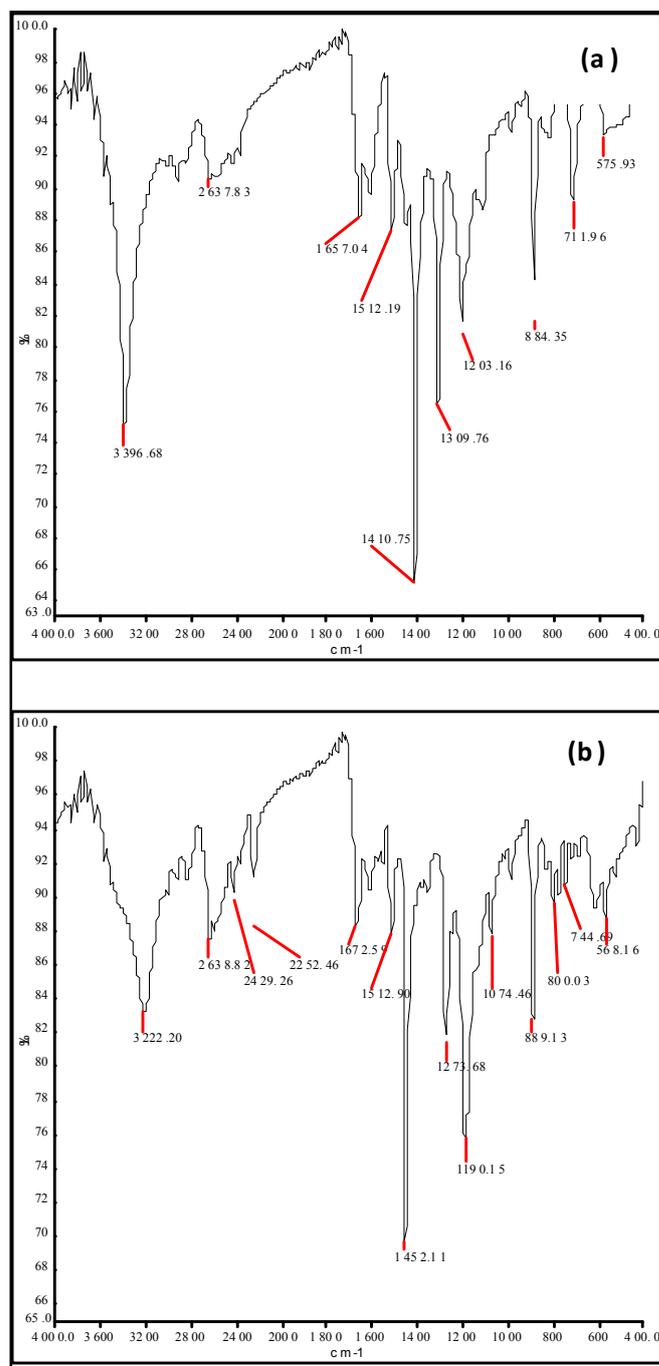


Fig. 2. Infrared spectra of (a) TMPD-Chloranil-I₂ and (b) TMPD-DDQ-I₂

The lower interband transitions with E_g=0.1175eV in DDQ complex and 0.122 eV in chloranil complex are forbidden indirect transitions obeying $\alpha h\nu = A(h\nu - E_g)^3$ (Figure 3(b) and 4(b)). Free carrier absorption is analyzed by plotting log α vs log λ (Figure 3(c) and 4(c)), which indicates scattering of charge carriers by acoustic phonons in chloranil complex and by impurity in DDQ complex, the later being due to the formation of semiquinone ions located at impurity sites. There are very low energy envelopes of rocking, wagging and group vibrations below 800 cm⁻¹ which have Gaussian shape in the chloranil complex and square-power beta density shape in the DDQ complex.

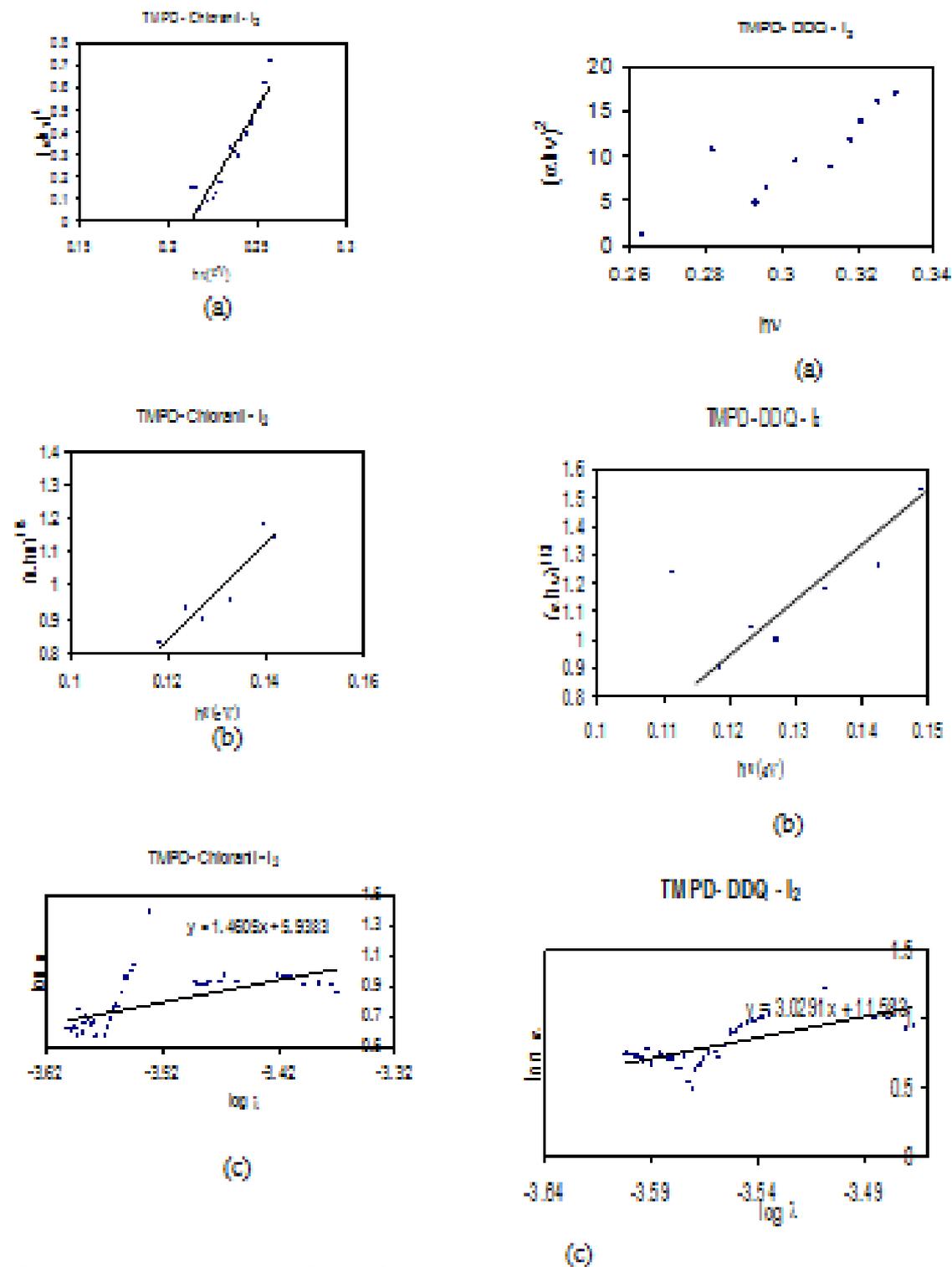


Fig. 3.(a) Upper absorption edge,(b) lower absorption edge and (c)free carrier absorption in TMPD-Chloranil-I₂

Fig. 4. (a) Upper absorption edge, (b) lower absorption edge and (c) free carrier absorption in TMPD-DDQ-I₂

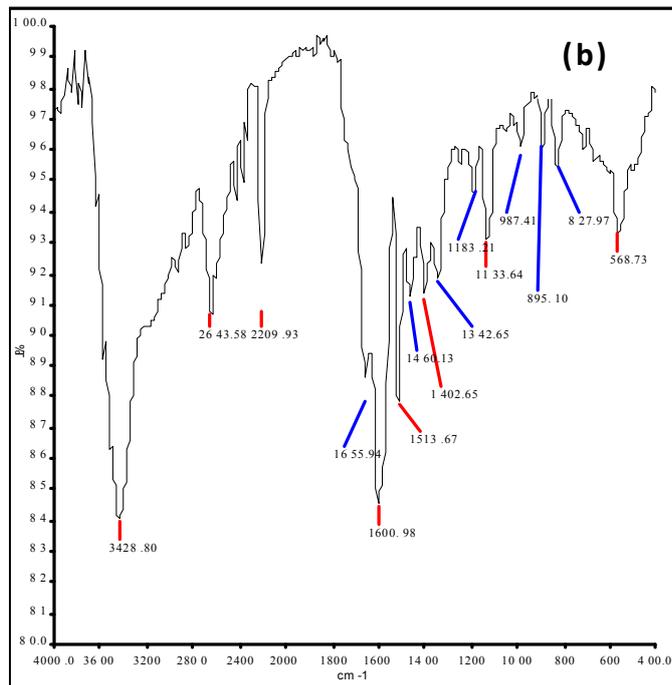
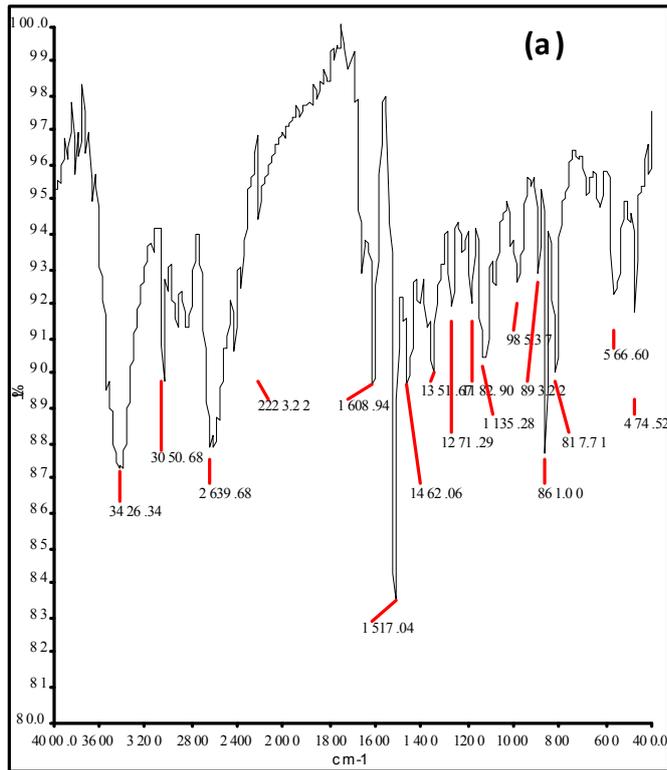


Fig. 5. Infrared spectra of
(a) TMPD-TCNQ-I₂ and
(b) TMPD-TCNE-I₂

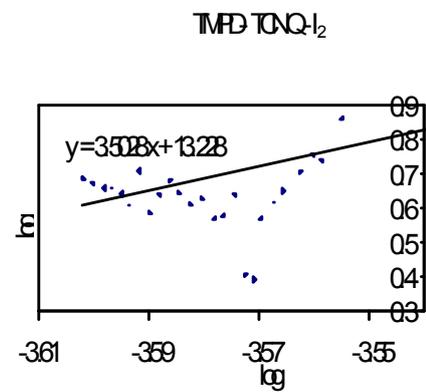
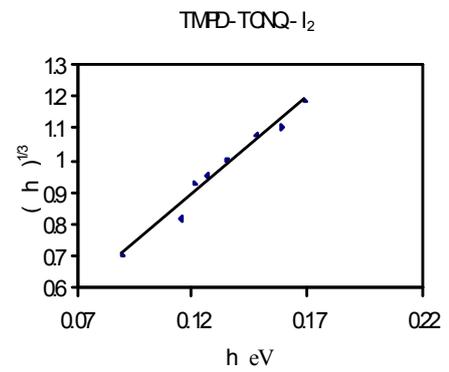
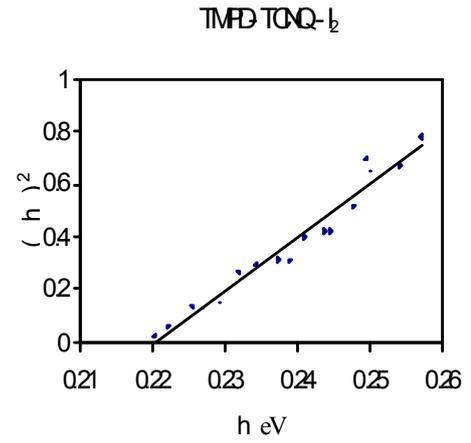


Fig. 6. (a) Upper absorption edge, (b) lower absorption edge and (c) free carrier absorption in TMPD-TCNQ-I₂

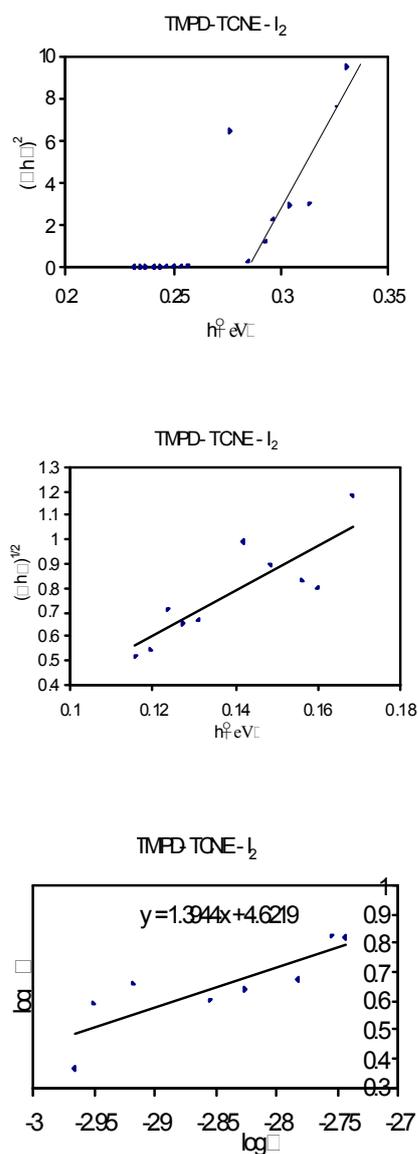


Fig. 7 (a) Upper absorption edge, (b) lower absorption edge and (c) free carrier absorption in TMPD-TCNE-I₂.

The lineshape in the chloranil complex reveals coupled low energy bands or electronic delocalization while the lineshape in the DDQ complex shows hopping mechanism of conduction due to somewhat larger intermolecular distance. Thus there are two Gaussian bands in the spectrum of chloranil complex revealing weaker molecular interactions and consequent delocalization of charge carriers. The neighbouring CDWs are incommensurate as well as suppression of Peierls transition leads to Gaussian delocalization. The infrared spectra of TMPD-TCNQ-I₂ and TMPD-TCNE-I₂ are also shown (Figure 5). Here the two absorption edges due to two interband transitions marked as NT-1 and NT-2 are clearly observed. The additional conduction band compared to a binary is an associated band edge (Pankove, 1971). The two absorption edges are fitted (Figure 6(a) and 7(a)). The upper edge in both

of the complexes fit $\alpha h\nu = A(h\nu - E_g)^{1/2}$ corresponding to allowed direct transition as found in the binary complexes of small organic donor and acceptor molecules. $E_g = 0.22 \text{ eV}$ for the TCNQ complex and $E_g = 0.275 \text{ eV}$ for the TCNE complex. The lower absorption edge is a forbidden indirect transition in the TCNQ complex obeying $\alpha h\nu = A(h\nu - E_g)^3$ with $E_g = 0.09 \text{ eV}$. The same edge in TCNE complex at $E_g = 0.12 \text{ eV}$ reveals an allowed indirect transition by obeying $\alpha h\nu = A(h\nu - E_g)^2$. Thus both of the band gaps are found to be larger for TCNE complex than those for TCNQ complex. (Figure 6 (b) and 7(b)). The TCNQ complex is also highly conducting than TCNE complex because of very small lower absorption edge of the order of 0.09 eV. The TCNQ complex is a small band gap semiconductor, although TCNE complex shows free-carrier absorption range. TMPD²⁺ dications are formed in both of the TCNQ and TCNE complexes. This is revealed by the absorption of dication bands. Free carrier absorption is analyzed by plotting $\log \alpha$ vs $\log \lambda$ (Figure 6(c) and 7(c)). Here also a difference is found between TCNQ and TCNE complexes. The TCNE complex revealed acoustic phonon scattering while TCNQ complex revealed impurity scattering. It may be that (TCNQ) sites or I₃-ions are scattering centers in the TCNQ complex. The acoustic phonon scattering reveals more conduction in TCNE complex. Finally, the electronic absorption envelope at very low frequency (below 800 cm⁻¹) has a Gaussian shape in the TCNE complex while the same has square-power beta density shape in the TCNQ complex. The envelope is broader in the TCNE complex than that in the TCNQ complex indicating stronger electron-phonon interaction in the TCNE complex than in the TCNQ complex. The four spectra of these four ternary complexes shows noise in the free-carrier absorption region above 3600 cm⁻¹ as expected in photoconductors and noise in the region of localization near the band edges. The TCNQ and TCNE complexes shows an asymmetric triangular distribution marked as T.D. in the mid-IR range due to either an internal Franz-Keldysh effect or due to imperfect nesting of the Fermi surface.

Conclusion

Although the TMPD- based ternary complexes are similar to benzidine-based ternary complexes as far as the two interband transitions are considered, the TMPD complexes are electrically more conducting than benzidine complexes. This can be concluded on the basis of free carrier absorption. More often, acoustic or optical phonons scatter charge carriers rather than impurity scattering as found in benzidine complexes.

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