CHAPTER 3

INFRARED SPECTRA OF TERNARY CTCs OF TMPD
3.1 INTRODUCTION:

Recently we have taken up the study of ternary charge transfer complexes based on standard organic donors and acceptors [1]. This study was inspired by the observation of superconductivity in the metal-ion based ternary complexes [2,3]. 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. [4,5]. 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 a1:2 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 3.1. TMPD forms many interesting and well-known CT complexes [6]. TMPD-chloranil is the complex studied rigorously as an organic semiconductor (7).

3.2 EXPERIMENTAL DETAILS:

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) obtained similarly were ground with TMPD in 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 compactions 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 4000 cm⁻¹.
3.3 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-I\textsubscript{2} and TMPD-DDQ are shown [Figure 3.2]. Both of them 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 $E_g = 0.22$eV for chloranil complex and $E_g = 0.24$eV for DDQ complex [figure 3.3(a) and 3.4(a)]. the lower interband transitions with $E_g = 0.112$eV in DDQ complex are forbidden indirect transitions obeying $\alpha h\nu = A(h\nu - E_g)^{3}$ [Figure 3.3(b) and 3.4(b)]. Free carrier absorption is analyzed by plotting log $\alpha$ vs log $\lambda$ [Figure 3.3(c) and 3.4(c)], which indicates scattering of charge carriers by acoustic phonons in chloranil complex and by optical phonons in DDQ complex, the later being due to the formation of semiquinone ions. There are very low energy envelopes of rocking, wagging and group vibrations below 800 cm\textsuperscript{-1} which have Gaussian shape in the chloranil complex and square-power beta density shape in the DDQ complex. 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 some what larger intermolecular distance.

The infrared spectra of TMPD-TCNQ-I\textsubscript{2} and TMPD-TCNE-I\textsubscript{2} are also shown [Figure 3.5]. 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 [9]. The two absorption edges are fitted
[Figure 3.6(a) and 3.7(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
\( E_g = 0.025 \text{eV} \). The same edge in TCNE complex at \( E_g = 0.11 \text{eV} \) 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 3.6 (b)
and 3.7(b)]. Free carrier absorption is analyzed by plotting log \( \alpha \) vs log \( \lambda \)
[Figure 3.6(c) and 3.7(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)\(^0\) sites or \( I_3 \)-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.

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Figure 3.1 molecular structures of organic donor and acceptors.
Figure 3.2 Infrared spectra of
(a) TMPD-Chloranil-I$_2$ and
(b) TMPD-DDQ-I$_2$
Figure 3.3  (a) Upper absorption edge,
(b) lower absorption edge and
(c) Free carrier absorption in TMPD-Chloranil-I$_2$
Figure 3.4  (a) Upper absorption edge,
(b) lower absorption edge and
(c) free carrier absorption in TMPD-DDQ-I$_2$
Figure 3.5 Infrared spectra of
(a) TMPD-TCNQ-I₂ and
(b) TMPD-TCNE-I₂

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Figure 3.6 (a) Upper absorption edge, (b) lower absorption edge and (c) free carrier absorption in TMPD-TCNQ-I₂
Figure 3.7 (a) Upper absorption edge, (b) lower absorption edge and (c) free carrier absorption in TMPD-TCNE-I$_2$. 

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3.4 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 found in benzidine complexes.
References: