CHAPTER 10

ANALYSIS OF INFRARED SPECTRA OF TERNARY CTCs BASED ON QUINOLINE-TRIETHYLAMINE COMBINATION
10.1 INTRODUCTION

The observation of unconventional density waves in ternary systems such as \( \alpha-(\text{BEDT-TTF})_2 \text{KHg (SCN)}_4 \) \([1,2]\) and unusual transport properties including superconductivity in ternary salts such as \( k-(\text{BEDT-TTF})_2 \text{Cu[N(Cu)}_2\text{]}\text{X} \) where \( X=\text{Cl, Br, I} \) \([3,4]\) led us to study the ternary charge transfer complexes \([5]\) and the present report is one of the series of recent studies. Currently, we divide ternary complexes in three sub-classes (1) one donor-two acceptors (2) two donors-one acceptor and (3) ternary involving at least one metal chelate as one of the three components. The last class may have two metal chelates or metal complex ions and only one organic cation or anion.

In the present work, we study infrared spectra of the ternary CTCs based on quinoline-triethylamine combination as two-donor systems. The main difference between one donor-two acceptor systems and two-donor-one acceptor systems lies in the fact that the former sub-class involves the presence of two conduction bands while the later sub-class involves electrostatic screening of charge transfer interaction by the additional donor. The properties (optical and transport) also depend on the geometrical shapes of the molecules, e.g. triethylammonium cation or \( \text{PF}_5^-, \text{ClO}_4^- \), etc. anions which have branched or global structure as compared to be flat molecules like perlene, \( \text{TMPD}^+ \) or \( \text{TCNQ}^- \) and DDQ'. This stereochemical effect is considered to be important in determining the electrical and optical properties of the ternary salts.

10.2 EXPERIMENTAL

The two donor-one acceptor ternary charge transfer complexes were prepared by homogeneously and microscopically mixing two donors namely triethylamine and quinoline (both in liquid forms) with standard organic acceptors such as chloranil (2,3,5,6- tetrachloro-p-benzoquinone), DDQ (2,3 – dichloro-5,6-dicyano-p-benzoquinone), TCNQ (7,7,8,8- tetracyano-p-quinodimethane), TCNE (\( N,N,N',N' \)-tetracyano-p-ethylene) and iodine in 1:1:2 molecular weight proportions. The three components were grinded for a long time in an eggate mortar with a pastle till the colours of the mixtures changed indicating the formation of charge transfer
complex in each case. The samples for studies in the form of circular pallettes were prepared by mixing only 5% of each complex with 95% of dry spectrograde KBr power in such a way that the specimens were semitransparent or translucent with negligible reflection. The spectra were recorded using a single beam Perkin-Elmer spectro-photometer in the full infrared range, i.e. 400 to 4000 cm⁻¹. The FTIR spectra thus recorded were having high resolution indicating even the fine structures of some important vibrational states. The molecular structures of the relevant organic molecules are shown (Figure 10.1)

\[
\begin{align*}
    & \text{(a)} \\
    & \text{(b)} \\
    & \text{(c)} \\
    & \text{(d)} \\
    & \text{(e)} \\
    & \text{(f)} \\
\end{align*}
\]

Figure 10.1

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10.3 RESULTS AND DISCUSSION:

The infrared spectra of the ternary complexes based on iodine, chloranil and DDQ in the full range, i.e. 400-4000 cm$^{-1}$, are shown (Figure 10.2). Other two spectra of TCNQ and TCNE are also shown in a separate figure (Figure 10.3). The Gaussian band and half-power beta density are shown with broken lines which are continuous absorption envelopes.

Consider triethylamine-quinoline-(chloranil)$_2$ ternary system. The analysis of the infrared spectrum shows a half-power beta density in high wavenumber range (Figure 10.4a) and a Gaussian envelope at low frequencies (Figure 10.4b). There are two optical absorption edges—one at $E_g=0.22$ eV and the another at 0.15 eV. The first one is allowed direct and the second one is forbidden direct (Figure 10.4c and 10.4a). $\alpha \hbar \nu$ is different from zero of $\hbar \omega = 4E_0 = 0.22$ eV revealing presence of exciton. This is describe by, [6]

$$\alpha (\Delta E_0) = \frac{4 \pi e^2}{m_0 c \omega m \left( \frac{2 \mu^*}{\hbar^2} \right)^{3/2}} \left| P_{nn}(0) \right|^2 \left( \frac{E^e_x}{E_1} \right)^{1/2}$$

Where $e$ is the electronic charge, $\mu^*$ is the effective reduced mass $m_0$ is the mass of electron, $c$ is the velocity of light, $n$ is the refractive index, $\hbar = \frac{\hbar}{2\pi}$ being the Planck's constant, $\left| P_{nn}(0) \right|$ is the probability of transition and as $E_1^{ex}$ tends to zero, $\alpha \sim (\hbar \omega - \Delta E_0)^{1/2}$. The above equation holds for direct transition. Similar theory of indirect exciton transitions has also been developed, which is applicable here. Thus the ternary complex behaves almost similar to binary complex revealing direct rather than indirect transitions. The unique range belonging to the absorption involving impurities is above $\hbar \omega > E_g$ where the free-carrier absorption is analyzed. Log $\alpha$ vs log$\lambda$ is plotted for a power low, since $\alpha_f \sim \lambda^{1.5}$ for scattering by acoustic phonons, $\alpha_t \sim \lambda^2$ for the Drude model for metals, $\alpha_t \sim \lambda^{2.5}$ for optical phonon scattering and $\alpha_t \sim \lambda^3$ or $\lambda^{3.5}$ for impurity scattering. [7]
The impurity absorption processes involve donor-acceptor pairs [8,9], band-filling effects like shrinkages of the direct and indirect gaps [10,11], isoelectronic traps [12], trivalent or pentavalent impurities [13,6], the decay of impurity wave function [14] impurity absorption due to transition between band and impurity level [15] presence of impurity sublattice [16], and free-carrier absorption [17]. The observation of one or more of the above mechanisms of absorption by electrons in the localized states in the organic semiconductor analogs would be quite interesting. The occupation of defects or dislocation centers by organic cations or anions in the weakly bound molecular crystals can provide absorption mechanisms described by impurity states.

The example of triethylammine-quinoline-(chloranil)_2 is very special in which the impurity absorption plays important role. This can be assigned to the weaker donor-acceptor interaction in the chloranil complex as compared to other ones studied in the present work. The effect of branched triethylammonium cations and the symmetric chloranil acceptor molecule which is less polarizable and less susceptible for quaternization and formation of semiquinone ion. The combined effect leads to the occupation of disordered sites by both donating cations. The free-carrier absorption analyzed by plotting log\(\alpha\) vs log\(\lambda\) provide two distinct ranges corresponding to \(\alpha_\lambda \sim \lambda^4\) at shorter wavelengths and \(\alpha_\lambda \sim \lambda^5\) at longer wave lengths. Thus the straight-line plots for power laws have slopes 3.8 and 5.2 at smaller and larger wave lengths respectively. (Figure 10.5 b and c).

The first power low (\(\alpha_\lambda \sim \lambda^4\)) can be obtained as a high energy (short-wavelength) approximation of an exact impurity absorption equation given by (6)

\[
\alpha = \frac{A N_{\text{loc}} (E_i / h\omega)^4}{E_i} \left[ \exp \left[ 4 \left( \frac{1 - E_i}{h\omega} \right) \tan^{-1} \left( \frac{1 - E_i}{h\omega} \right) \right] \right] \left[ 1 - \exp \left[ 2\pi \left( \frac{E_i}{h\omega} - 1 \right) \right] \right] \]

Where \(N_{\text{loc}}\) is the concentration of localizing impurities, \(E_i\) is the impurity ionization energy, \(h\omega\) is the photon energy and \(A\) is a constant. The factor \(\left( \frac{E_i}{h\omega} \right)^4\) provides \(\lambda^4\)
dependence because of $\omega=\frac{2\pi c}{\lambda}$ when the other frequency-dependent factor becomes constant in high-frequency limit. The above equation is based on the theory of radiation (absorption) from the localized states with a hydrogen-like spectrum. Thus the absorption depending on $\lambda^4$ can be assigned to (TETQ$^+$) radicals which provide a positively-charged ions involved like ionized hydrogen.

The second power low ($\alpha\sim\lambda^5$) can be obtained as high energy (short wavelength) approximation of one more exact impurity absorption equation given by (6)

$$\alpha \equiv \frac{\hbar \omega - E_1}{\hbar^2 \omega^2 \left[ \hbar^2 \chi^2 + 2m^*(\hbar \omega - E_1) \right]^{\frac{1}{4}}}$$

Where $\chi$ is defined by the impurity wave function described by

$$\varphi_I = \frac{1}{2\chi} \frac{1}{\hbar} e^{\frac{i}{\hbar} E_{\text{loc}} t}$$

In which $c$ is a constant, $\rho = |r - R_{\text{loc}}|$ and $E_{\text{loc}}$ being the energy of localization level. $1/2\chi$ measures the distance at which the probability of locating the electron reduces by $1/e$ factor. $\chi$ plays the role of a wave-vector because the band maximum is at a frequency given by

$$\hbar \omega = E_1 + \frac{\hbar^2 \chi^2}{8m^*}$$

Where $m^*$ is the effective mass. The high frequency limit when $\hbar \omega >> E_1$ in eqn. (3) provides

$$\alpha \equiv A \omega^{-5} = A \left( \frac{2\pi c}{\hbar} \right)^{-5} \lambda^5$$

This is the dependence found in log $\alpha$ vs log $\lambda$ plot (Figure 10.5 b). The absorption spectrum should be comparatively wide but never the less a finite band. This absorption is due to impurity band formed by the sublattice of quinolinium cations.

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Next is the scope for analysis of IR spectrum of triethylamine-quinoline-(DDQ)$_2$. The entire infrared range includes subranges of two optical absorption edges which show allowed indirect transitions (Figure 10.6a and b). Other two ranges above the band gaps reveal optical phonon scattering in high energy range and acoustic phonon scattering in low energy range (Figure 10.6 c and d). The DDQ complex out of five complexes studied here show scattering of charge carriers by acoustic phonons indicating that the electrical conductivity is expected to be highest. The optical phonon scattering is indicative of the dative binding and ionic nature of the ternary salt because of the formation of semiquinone ion due to asymmetric and polarizable DDQ molecule. Probably more than that is the effect of negative and reversible polarographic half-wave potential of DDQ studied with electrochemical polarography because this ionic effect is also found in TCNQ molecule which is symmetric and consequently less polarizable.

The infrared spectrum of tricthylamine-quinoline-2I$_2$ is also similarly treated for quantitative analysis. A half-power beta density resulting from hopping transport found in a small range (Figure 10.7a). Another range reveals Gaussian distribution due to the Doppler broadening and consequent electronic delocalization (Figure 10.7b). The infrared absorption edge about $E_g=0.115$eV is observed at a rather lower value of energy as compared to usual Peierls gap and band gaps observed in other ternary salts. Therefore, this can be assigned to a band gap along the polyiodine chains with charge transfer. However, the band gap remains forbidden direct gap as in the binary salts (Figure 10.7 c). The analysis of scattering mechanism for free charge carriers shows an ionized impurity mechanism governing the absorption related with the formation of $I_3^-$ ions. Although neutral impurities giving rise to $\alpha_\lambda \sim \lambda^3$ and negatively ionized impurities giving rise to $\alpha_\lambda \sim \lambda^{3.5}$ can be distinguished by the more accurate data and vigilant comparison of the slopes of log $\alpha$ vs log $\lambda$ for a large number of inorganic and organic semiconductors, a continuous variation from 3.0 to 3.5 values of slopes presently makes it somewhat difficult to come to any definite conclusion about this open problem.

The further analytical work is carried out using the spectrum of triethyl-amine-quinoline-(TCNQ)$_2$ (Figure 10. 8). Here the electronic delocalization energy range is...
found by plotting Gaussian curve and analyzing it and the localization range is found by fitting a half-power beta density which requires hopping mechanism because of larger intermolecular distance created by the steric effect of three-dimensional triethylammonium cations. (Figure 10.8a & b).

The free-carrier absorption is governed by the collisions of optical phonons and charge carriers (Figure 10.8c). This is due to $\pi$-electron accepting nature of $C \equiv N$ and electron \text{-IMV} (intramolecular vibration) coupling as well as negative and reversible polarographic half-wave potential of TCNQ- anions.

The last is the case of the TCNE salt, i.e. triethylamine-quinoline-(TCNE)$_2$ which is again analyzed similarly revealing half-power beta density (Figure 10.9a), Gaussian profile (Figure 10.9b), a direct forbidden transition (Figure 10.9c) and impurity scattering in the conduction band (Figure 10.9d). The optical absorption edge provides a slightly larger value of the band gap ($E_g \equiv 0.31$eV) than the usual Peierls gap. This is consistent with the weaker interaction of donors and acceptor molecules in the TCNE ternary salt. The impurity scattering resulting from disordered sites of TCNE$^-$ anions due to their interaction with two rather than one specific cation.

Details of infrared absorption edges, free-carrier absorption and the two absorption envelops are all summarized (Table 10.1 to 10.3)
Figure 10.2 Infrared spectra of (a) TEtA-Qn-(CA)$_2$ (b) TEtA-Qn-(DDQ)$_2$ (c) TEtA-Qn-2I$_2$
Figure 10.3 Infrared spectra of (a) TET-A-Qn-(TCNQ)$_2$ and (b) TET-A-Qn-(TCNE)$_2$
Figure 10.4 Analysis of the spectrum of TET-A-Qn-(CA)₂ (a) Half-power beta density (b) Gaussian band (envelope) (c) Direct transition (allowed) with $E_g = 0.22$ eV
Figure 10.5 Further analysis of the spectrum of TET-A-Qn-(CA)$_2$

(a) Direct transition (forbidden) with $E_g=0.15$ eV

(b) Impurity band scattering with $\alpha_l \sim \lambda^5$

(c) Discrete impurity level scattering with $\alpha_l \sim \lambda^4$
Figure 10.6 Analysis of the spectrum of TETA-Qn-(DDQ)$_2$

(a) Allowed indirect transition with $E_g = 0.07$ eV
(b) Allowed indirect transition with $E_g = 0.21$ eV
(c) Free-carrier absorption due to acoustic phonons
(d) Free-carrier absorption due to optical phonons
Figure 10.7 Analysis of the spectrum of TEtA-Quinoline-(l2)

(a) Half-power beta density
(b) Gaussian envelope
(c) Forbidden direct transition with $E_g=0.11\,\text{eV}$
(d) Free-carrier absorption due to impurities
Figure 10.8 Analysis of the spectrum of TEtA-Quinoline-(TCNQ)$_2$

(a) Gaussian envelope  
(b) Half-power beta density  
(c) Free-carrier absorption due to optical phonons
Figure 10.9 Analysis of the spectrum of TEtA-Quinoline-(TCNE)$_2$

(a) Half-power beta density
(b) Gaussian envelope
(c) Forbidden direct transition with $E_g = 0.29$eV
(d) Free-carrier absorption due to impurities.
Table 10.1 Infrared absorption edges in the spectra of the ternary systems based on triethylamine-quinoline combination.

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Absorption function</th>
<th>Type of transition</th>
<th>Value of band gap $E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEtA-Qn-chloranil</td>
<td>$\alpha h\nu=A(h\nu-E_a)^{1/2}$</td>
<td>Allowed direct</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$\alpha h\nu=A(h\nu-E_a)^{3/2}$</td>
<td>Forbidden direct</td>
<td>0.15</td>
</tr>
<tr>
<td>TEtA-Qn-DDQ</td>
<td>$\alpha h\nu=A(h\nu-E_a)^2$</td>
<td>Allowed indirect</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>$\alpha h\nu=A(h\nu-E_a)^2$</td>
<td>Allowed indirect</td>
<td>0.07</td>
</tr>
<tr>
<td>TEtA-Qn-I$_2$</td>
<td>$\alpha h\nu=A(h\nu-E_a)^{3/2}$</td>
<td>Forbidden direct</td>
<td>0.11</td>
</tr>
<tr>
<td>TEtA-Qn-TCNQ</td>
<td>Not observed</td>
<td>Not observed</td>
<td>Not observed</td>
</tr>
<tr>
<td>TEtA-Qn-TCNE</td>
<td>$\alpha h\nu=A(h\nu-E_a)^{3/2}$</td>
<td>Forbidden direct</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 10.2 Free-carrier absorption in the ternary complexes based on triethylamine-quinoline combination.

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Range of wave number (cm$^{-1}$)</th>
<th>Slope of log $\alpha$ vs log $\lambda$</th>
<th>Scattering mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEtA-Qn—chloranil</td>
<td>2175-2465</td>
<td>4.8</td>
<td>Impurity band scattering</td>
</tr>
<tr>
<td></td>
<td>2579-3057</td>
<td>3.9</td>
<td>Positively charged impurity scattering</td>
</tr>
<tr>
<td>TEtA-Qn—DDQ</td>
<td>1564-2381</td>
<td>1.2</td>
<td>Acoustic phonon scattering</td>
</tr>
<tr>
<td></td>
<td>2527-3214</td>
<td>2.5</td>
<td>Optical phonon scattering</td>
</tr>
<tr>
<td>TEtA-Qn—I$_2$</td>
<td>1910-2453</td>
<td>2.8</td>
<td>Neutral Impurity scattering</td>
</tr>
<tr>
<td>TEtA-Qn—TCNQ</td>
<td>2879-3245</td>
<td>2.2</td>
<td>Optical phonon scattering</td>
</tr>
<tr>
<td>TEtA-Qn—TCNE</td>
<td>2879-3464</td>
<td>3.5</td>
<td>Negatively charged impurity scattering</td>
</tr>
</tbody>
</table>
Table 10.3 Types and parameters of the electronic absorption envelopes in the IR spectra of the ternary complexes based on triethyl-amine-quinoline combination.

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>First envelope</th>
<th>Second envelope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ko (cm(^{-1}))</td>
<td>(\delta K) (cm(^{-1}))</td>
</tr>
<tr>
<td>TEtA -Qn-chloranil</td>
<td>3000</td>
<td>2400</td>
</tr>
<tr>
<td></td>
<td>(Half power beta density)</td>
<td>(Gaussian distribution)</td>
</tr>
<tr>
<td>TEtA -Qn-DDQ</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TEtA -Qn—I(_2)</td>
<td>3000</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>(Half power beta density)</td>
<td>(Gaussian distribution)</td>
</tr>
<tr>
<td>TEtA -Qn-(TCNQ)</td>
<td>2200</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>(Half power beta density)</td>
<td>centrally-split</td>
</tr>
<tr>
<td>TEtA -Qn-TCNE</td>
<td>3300</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>(power beta density)</td>
<td>(Asymmetric Gaussian distribution)</td>
</tr>
</tbody>
</table>

10.4 CONCLUSION:

The half-power beta distributions observed in the absorption spectra of four out of five (Excepting DDQ based salt) complexes are consistent with the randomization of the ionic sites arising from the steric effect of non-planar and branched triethylammonium cations. Stronger dependences of absorption of wavelengths (\(\alpha_t \sim \lambda^4\) or \(\alpha_t \sim \lambda^5\)) in TEtA-Qn-(Chloranil)\(_2\) are explained on the bases of high energy limits of the impurity absorption for hydrogen-like levels and for finite bands, formed particularly by positively charged impurities rather than usual negative impurity.
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