CHAPTER 8

INFRARED SPECTRA OF TERNARY COMPLEXES USING BENZIDINE AND QUINOLINE AS DONORS
8.1 INTRODUCTION

The earlier studies on ternary organic CT complexes included doped (TMTSF)$_2$ ClO$_4$, alkyl-ammonium donors with TCNQ-iodine, pyrene-TCNQ-ferrocene, substituted anthraquinone complexes and others [1-6]. (TMPD)$_{1.5}$ --KI-I$_2$ and (TMPD)$_{1.5}$ --HI-I$_2$ can be also considered as ternary systems [7].

There are two types of ternary systems. (1) one-donor and two-acceptor based systems which include, K-(BEDT-TTF)$_2$ Cu[(CN)$_2$]NX where X=Cl, Br, I, (C$_1$-TET-TTF)(FeBr$_4$)$_{1-x}$ FeCl$_4$)$_x$ etc. [8-15] some of which are organic superconductors. (2) Two-donors and one acceptor based systems including \(\alpha\)-(BEDT-TTF)$_2$MHg(SCN)$_4$ where M=K,NH$_4$, \(\alpha\)-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and \(\beta\)-(CH$_3$)$_4$AS[Pd(dmit)$_2$] [16-23], some of which were also superconducting.

Ternary charge transfer complexes and radical-ion salts possess unique physical properties which are absent in binary (bimolecular) complexes. These properties include two-band transport, commensurate-to incommensurate transition, alloy properties, cooperative and competitive binding, more than two oscillator models or three absorption envelopes, complex-salt character and electron-exciton interactions.

In the present work, we report CT complexes of benzidine-quinoline-TCNQ,benzidine-quinoline-TCNE, benzidine-quinoline-chloranil,benzidine-quinoline-DDQ and benzidine-quinoline-I$_2$ all in 1:1:2 molecular weight proportions.

8.2 EXPERIMENTAL

The donor benzidine was grinded with acceptors like TCNQ(7,7,8,8-tetra-cyano-p-quinodimethane), TCNE(N,N',N'-tetracyano-p-ethylene), chloranil (2,3,5,6-tetrachloro-p-benzoquinone), DDQ(2,3-dichloro-5,6-dicyano-p-benzoquinone) and iodine in 1:2 molecular weight proportions. The liquid donor quinoline was added with the help of micropipette in a few drops needed in molecular weight proportions to form the ternary complexes.
The infrared spectra were recorded using a standard Perkin-Elmer spectrophotometer on the KBr-based semi-transparent pellets of all the five ternary complexes.

8.3 RESULTS AND DISCUSSION

The first is the infrared spectrum of benzidine-quinoline-TCNQ which is shown here (Figure 8.1a). This spectrum can be divided in two parts according to background absorption governed by electronic absorption. The first range is the 1700-3600 cm\(^{-1}\) where a very broad half-power beta density distribution is observed given by

\[
\alpha = \alpha_0 E^{1/2} (1-E^*)^{1/2}
\]

(8.1)

Where \( E^* = (b-a)/b \) is the reduced, dimensionless energy variable. But difference in the spectrum between this and that of benzidine-pyridine-TCNQ reported recently is in the splitting of the above distribution at 2217 cm\(^{-1}\) by a dispersion shape of \( \varepsilon_1(\omega) \) the real part of dielectric constant. Because of this splitting the distribution becomes asymmetric below 217 cm\(^{-1}\). The range 1700-2170 cm\(^{-1}\) correspond more to a transition across the usual band gap around 1700 cm\(^{-1}\), rather than being a part of beta density. This splitting and asymmetry arise from stronger interaction between quinoline and TCNQ than pyridine-TCNQ interaction. The second part is below 1700 cm\(^{-1}\) down to 500 cm\(^{-1}\). This range consists of a very broad symmetric Gaussian band around 1100 cm\(^{-1}\). There are no two envelopes below 1700 cm\(^{-1}\). The lowest frequency Gaussian peak around 700 or 750 cm\(^{-1}\) is merged into the mid-IR envelope. This also is a consequence of strong interaction between quinoline and TCNQ. The second spectrum is that of benzidine-quinoline-DDQ (Figure 8.1 b). Here two the spectrum can be divided in two main parts. The first range is above 1800 cm\(^{-1}\) where a very large triangular distribution centered around 3082 cm\(^{-1}\) is observed. This is a consequence of screening of interaction between benzidine and DDQ by quinoline. In this range, spectrum significantly differs from that of TCNQ complex. This arises from asymmetric nature of DDQ molecule leading to more electronic molecular polarizability. It can not be attributed to the halogen end-group interacting with donor because iodine complex
shows different features in this range. The second range is below 1800 cm\(^{-1}\) down to 400 cm\(^{-1}\). The background absorption is a monotonic function rather than a Gaussian distribution, the later found in the TCNQ complex. The absorption decreases as the frequency (or energy) decreases. The absorption is minimum at or below 0.05 eV (400 cm\(^{-1}\)). Thus in the both ranges spectrum differs for DDQ complex from that of the TCNQ complex. Benzidine-DDQ interaction is stronger than benzidine-TCNQ interaction. Benzidine is enable to screen strongly in the DDQ complex. There is a steep rise above 1560 cm\(^{-1}\) towards the high frequency side. The absorption is minimum near 1750 cm\(^{-1}\) and there is a long band-tailing towards high frequency side. This may be related with imperfect nesting leading to this feature [24].

The real part of optical conductivity \(\sigma_1(\omega)\) and the imaginary part of dielectric constant \(\varepsilon_2(\omega)\) are related if we look at the high-frequency behaviour, it is a broad dispersion shape between 3600 cm\(^{-1}\) and 1750 cm\(^{-1}\). The constant high frequency background above 3600 cm\(^{-1}\) is extrapolated and considered to be zero level, the curve in 1750 – 3600 cm\(^{-1}\) is cut to give a dispersion shape governed by \(\varepsilon_1(\omega)\). There is anomalous dispersion in this range. It is a fluctuation in absorption around zero level and if we apply lever rule, there is no net absorption. The integration (area under the band) is almost zero in this range.

The second range of absorption below 1560 cm\(^{-1}\) mainly consists of absorption across a very small band gap (\(E_g < 0.05\) eV). These transitions coupled two bands through a Gaussian distribution in the TCNQ salts. The transitions are hindered in TCNQ complex while the transitions occur without being screened in the DDQ complex. In both of TCNQ and DDQ complexes, the lowest-lying envelope around 750 cm\(^{-1}\) is not observed because it merges in the mid-IR envelope.

The third spectrum is that of benzidine-quinoline-chloranil (Figure 8.2 a). In this case, three envelopes are observed because of lack of delocalization due to screening effect. Benzidine-chloranil binary complex is weaker in interaction than benzidine-DDQ binary complex. As a result, the interaction is screened by quionoline molecules. The highest-lying envelope is somewhat similar to the one found in the TCNQ complex but somewhat asymmetric rather than symmetric with more absorption on high-frequency side. This is between 1800 cm\(^{-1}\) and 3600 cm\(^{-1}\).
The mid-IR envelope between 1100 cm\(^{-1}\) and 1800 cm\(^{-1}\) is a flat beta density peak following a half-power law as given by equation 1. In this case, sharp bands are neglected and either background is considered or inflexion points of the spikes are joined. The lowest lying Gaussian-shaped envelope around 750 cm\(^{-1}\) is clearly seen. Thus the spectrum is similar to that of benzidine-pyridine-chloranil.

The next is the IR spectrum of benzidine-quinoline-TCNE (Figure 8.2b). The interaction is stronger than in the chloranil complex. The high-frequency envelope above 1800 cm\(^{-1}\) is a triangular envelope associated with imperfect nesting as observed in the DDQ complex. This similarity reveals that this special spectral feature arises out of molecular polarizability of TCNE. TCNE does not contain aromatic ring as in TCNQ and contains C=C bridge. The four cyano-groups are more flexible and rotatable in three-dimensions leading to orientational polarizability. These rotations are hindered by the charge cloud of aromatic ring in TCNQ.

The mid-IR envelope between 950 cm\(^{-1}\) and 180 cm\(^{-1}\) is highly asymmetric with low-frequency tailing as compared to the envelope of chloranil complex. The lowest-lying envelope between 400 cm\(^{-1}\) and 900 cm\(^{-1}\) shows a similar asymmetric distortion compared to that in the case of chloranil complex.

The last spectrum of benzidine-quinoline-iodine is also shown (Figure 8.2c). This spectrum is similar to its pyridine analog above 1700 cm\(^{-1}\). The range below 1700 cm\(^{-1}\) consists of a large number of absorption bands but leaving a scope for the background absorption which increases as the frequency decreases. This may correspond to a negative band gap as in semi-metals or free-carrier absorption above a very small band gap lying in far-infrared range. Also there is a possibility of a transition to an impurity level [25].
Figure 8.1 Infrared spectra of
(a) benzidine-quinoline-TCNQ and
(b) benzidiene-quinoline-DDQ

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Figure 8.2  Infrared spectra of
(a) benzidine-quinoline-chloranil
(b) benzidiene-quinoline-TCNE and
(c) benzidiene-quinoline-iodine
Figure 8.3  
(a) Beta density fit  
(b) Gaussian fit and  
(c) Nature of transition above 0.2 eV gap  
--- all of the TCNQ complex
Next is the analysis of spectrum of benzidine-quinoline-DDQ. The analysis indicates that the higher transition across the gap of about 0.2 eV is forbidden direct and the lower transition across the gap of nearly 0.05 eV is indirect and forbidden type. The lower band gap can be assigned to the quinoline-DDQ interaction because it is not found in the spectrum of binary benzidine-DDQ system. This analysis is shown (Figure 8.4 a and b)

Similar analysis of the nature of transition for the chloranil complex is also carried out (Figure 8.5 a). An allowed direct transition is evident. The high-frequency and mid-IR envelopes are both beta distribution with half-power beta density (Figure 8.5b and c). The lowest-frequency envelope is analyzed to be Gaussian curve (Figure 8.5d).

More strongly interacting TCNE-based ternary complex shows two band gaps of 0.2 eV and 0.1 eV with corresponding forbidden indirect and allowed indirect transitions, respectively (Figure 8.6 a and b).

The analysis of the last spectrum of benzidine-quinoline-iodine complex reveals an allowed direct transition (Figure 8.7a) and two Gaussian envelopes (Figure 8.7 b and c).

Details of upper and lower absorption edges and both absorption envelopes are summarized (Table 8.1 & 8.2)
Figure 8.4  (a) Nature of transition above 0.2 eV gap and  
(b) nature of transition above 0.05 eV gap
**Figure 8.5**

(a) Nature of transition above 0.225 eV gap  
(b) beta density peak  
(c) second beta density peak and  
(d) Gaussian fit
Figure 8.6 (a) nature of transition above 0.1 eV gap and (b) nature of transition above 0.2 eV gap
Figure 8.7  (a) Nature of transition above 0.21 eV gap 
(b) The first Gaussian peak and 
(c) the second Gaussian peak
Table 8.1 Infrared absorption edges for the ternary complexes based on benzidine-quinoline combination

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Upper edge</th>
<th>Lower edge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbtion function</td>
<td>Type of transition</td>
</tr>
<tr>
<td>Benzidine-quinoline-TCNQ</td>
<td>$\alpha \nu = A(h\nu - E_g)^{1/2}$</td>
<td>Allowed direct</td>
</tr>
<tr>
<td>Benzidine-quinoline-DDQ</td>
<td>$\alpha \nu = A(h\nu - E_g)^{3/2}$</td>
<td>Forbidden direct</td>
</tr>
<tr>
<td>Benzidine-quinoline-chloranil</td>
<td>$\alpha \nu = A(h\nu - E_g)^{1/2}$</td>
<td>Allowed direct</td>
</tr>
<tr>
<td>Benzidine-quinoline-TCNE</td>
<td>$\alpha \nu = A(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
</tr>
<tr>
<td>Benzidine-quinoline-I$_2$</td>
<td>$\alpha \nu = A(h\nu - E_g)^{1/2}$</td>
<td>Allowed direct</td>
</tr>
</tbody>
</table>
Table 8.2 Types and parameters of electronic absorption envelopes in the spectra of ternary complexes based on benzidine-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>$K_0$ (cm$^{-1}$), $\delta K$ (cm$^{-1}$), $\alpha_m$ (%)</td>
<td>$K_0$ (cm$^{-1}$), $\delta K$ (cm$^{-1}$), $\alpha_m$ (%)</td>
</tr>
<tr>
<td>Benzidine-quinoline-TCNQ</td>
<td>2800 1300 30% (Half power-Beta density)</td>
<td>1100 1050 35% (Gaussian distribution)</td>
</tr>
<tr>
<td>Benzidine-quinoline-DDQ</td>
<td>3200 1100 50% (Triangular distribution)</td>
<td>- - -</td>
</tr>
<tr>
<td>Benzidine-quinoline-chloranil</td>
<td>2800 1700 20% (Half-power beta density)</td>
<td>770 600 16% (Gaussian distribution)</td>
</tr>
<tr>
<td></td>
<td>1400 800 16% (Half power beta density)</td>
<td></td>
</tr>
<tr>
<td>Benzidine-quinoline-TCNE</td>
<td>3200 1200 45% (Triangular distribution)</td>
<td>- - -</td>
</tr>
<tr>
<td>-Benzidine-quinoline-iodine</td>
<td>2800 1700 25% (Gaussian distribution)</td>
<td>850 800 20% (Gaussian distribution)</td>
</tr>
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</table>

8.4 CONCLUSION:

The three out of five ternary complexes based on TCNQ, DDQ and iodine show unusual spectral features which are making use of benzidine-quinoline combination. The TCNQ complex shows merging of two lower envelopes with unusually broad Gaussian band DDQ complex shows two triangular distribution related with imperfect nesting. TCNE and chloranil show three envelopes related with three band model. Iodine complex seems to be having highest conductivity because of negative band gap or free-carrier absorption.
References:


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