Chapter – 10

FTIR Spectroscopy of charge transfer Complexes of

Bis (Ethylenedithiolo) Tetrathaifulvalene
1. Introduction:

There is enormous interest in carrying out research work on the charge transfer complexes (CTCS) and radical – ion salts of electron donors arising from organo – sulfur chemistry. The best known among these are CTCS of TTF and TSeF based organic conductors which are found to be metallic at room temperature. Some of them even become superconducting at low enough temperatures. These conductors are known as Bechgaard salts including TTF, TSeF, TMTTF, TMTSF, HMTTF, HMTSF, etc. salts with negative ions like ClO$_4^-$, NO$_3^-$, PF$_6^-$, BF$_4^-$, AsF$_6^-$, etc. These also became as A$_2$B salts where A = TMTSF or TMTTF which shows charge ordering transition. Others organo sulfur or selenium donors are such as BEDT – TTF (ET) and BEDT–TSeF (BETS) where BEDT–TTF = bis (ethylenedithio trtrathiafulvalene and BEDT – TSeF = bis (ethylenedithio) tetraselenafulvalene). Charge order – disorder phase transition was found in ($\alpha'$ – BEDT – TTF)$_2$ Br$_2$ (1). Density wave instability in $\alpha$ – (BEDT – TTF)$_2$ KHg(SCN)$_4$ was studied through X – ray diffuse scattering (2). Orbital effect of magnetic field on low temperature phase of $\alpha$ – (BEDT–TTF)$_2$ KHg(SCN)$_4$ was studied (3). Super conductivity and localization in density wave state were investigated for $\alpha$ – (BEDT–TTF)$_2$ MHg(SCN)$_4$ salts (4). Collective excitations in charge – ordered phase of $\alpha$ – (BEDT–TTF)$_2$ I$_3$ were reported (5). Electric field induced lifting of degeneracy in Dirac – like Landau levels was found in $\alpha$ – (BEDT – TTF)$_2$ I$_3$ (6). Charge
transfer complexes of BEDT–TTF with \([ \text{Re}_2(\text{SCN})_{10}]^{2–,–3}\) ions were studied (7). \((\text{BEDT–TTF})_4\text{Fe(NCS)}_6\text{CH}_2\text{Cl}_2\) and \((\text{BEDT – TTF }\)\text{Cr(NSC)}_4\text{bipyrimidine} were also prepared (8). Structures of \((\text{BEDT–TTF})_2\text{M}_6\text{O}_{19}\) where \(\text{M} = \text{Mo}, \text{W}\) were resolved (9). Synthesis, crystal structure and properties of BEDT–TTF charge transfer salt with[\text{Mo}_3\text{S}_7\text{Br}_6]^{2–} cluster were studied (10). BEDE–TTF complex with ion such as \((\text{Br}_2)_{0.2}\) \((\text{Br I Cl})_{0.1}\) \((\text{Cl}_2)_{0.7}\) was found to be metallic (11). Molecular charge transfer salt of BEDT –TTF with the oxalate – bridged dimeric anion \(\text{Fe}_2(\text{C}_2\text{O}_4)_5^{4–}\) has also been prepared (12). Polarized reflectance spectra of \(\beta–(\text{BEDT–TTF})_2\) \text{I Be}_2\) were studied (13). An organic metal was found which was \((\text{BEDT – TTF }\)\text{BF}_4\text{CH}_3\text{CN}\) (14). Charge transfer compounds of BEDT–TTF with copper halides were prepared (15). The complexes like \((\text{BEDT – TTF})_2\) \text{Cu}[\text{N(CN)}_2]\text{Br}\) and \((\text{BEDT – TTF})_2\) \text{Cu(NCS)}_2\) were also studied in detail (16). Infrared and Raman study of charge –ordered state of \(\alpha–(\text{ET})_2\) \text{Cu}_2\text{CN}_2[\text{N(CN)}]_2\) was carried out (17). High pressure study of \(\beta’(\text{ET})\) \text{(TCNQ)} was carried out (18). Dynamical charge disproportionation in metallic state \(\alpha–(\text{BEDT – TTF })_2\) \text{RbZn (SCN)}_4\) was found (19). A similar study was also carried out on \(\alpha–(\text{BEDT – TTF })_2\) \text{I}_3\) (20). Molecular materials based on ET and \([\text{M(tdas)}_2]\) where \(\text{tdas} = 1,2,5 – \text{dithiazole} – 3,4 \text{ dithiolenes}\) were also prepared and their conductivity were studied (21). A new salt of BEDT –TTF with photosensitive \([\text{RuCl}_5(\text{NO})]^{2–}\) was also synthesized and studied (22). Finally, organic metals and superconductors based on \((\text{BEDT – TSeF})\) or BETS were reviewed (23).
2. Experimental:

BEDT–TTF [bis (ethylenedithio trathiafulvalene] was obtained in pure form from Aldrich-Sigma chemical company and was taken in 1:1 molecular proportion with organic with acceptors such as TCNQ (7,7,8,8 – tetracyano – p – quino – dimethane), TCNE (tetracyano – p – ethylene ), DDQ (2,3 – dichlоро – 5,6 – dicynо – p – benzoquinone), Chloranil and iodine. BEDT –TTF the mixture was grinded till the colour deepened or changed. The CTCS thus formed were mixed in 5% with 95% KBr powder which was anhydrous prepared by using a manuiltlu operated compressing machine. These pellets were placed in the dark chamber of spectrophoto meter.

The spectra in the range 400 – 4000 cm\(^{-1}\) were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin Elmer Comnpy, USA having a resolution of 0.15 cm\(^{-1}\), a scan range of 15,000 – 30cm\(^{-1}\), a scan time of 20 scan/sec, an OPD velocity of 0.20 cm/sec and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800 cm\(^{-1}\) – 370 cm\(^{-1}\). The spectra were recorded in purge mode.
3. Results and Discussion:

The molecular structures of BEDT–TTF and organic acceptors are shown in (Figure 1). The FTIR spectrum of BEDT–TTF is shown (Figure 2a) which contains arrange of half power beta density obeying

\[ \alpha = \alpha_0 + \alpha_1 K^{1/2} (1 - K^*)^{1/2} \]

a range of gaussian band in mid–IR range and a Lorentzian profile in low frequency range. The half –power beta density is related with hopping transport of charge carriers. The gaussian band can be attributed to delocalization of charge carriers. He Lorentzian curve at low frequency can be assigned to an oscillator model. The beta density is fitted (Figure 2b) and the gaussian band is also fitted (Figure 2c).

The FTIR spectrum of TCNQ complex of BEDT–TTF is shown (Figure 3a). A half –power beta density associated with hopping conduction is spreader over the entire infrared range. This beta density is fitted on one side (Figure 3b). The long range beta density reveals that the hopping conduction is enhanced by BEDT–TTF–TCNQ shows layers of BEDT–TTF molecules leaving a cylindrical cavity for TCNQ molecules. Nearly two – dimensional nature of spectrum shows that the main conduction is due to BEDT–TTF molecules arranged in layers.

The FTIR spectrum of TCNE complex of BEDT–TTF is shown (Figure 4a). This contains a sharp oscillator function around 3412 cm\(^{-1}\), a range of nature of interband transition below 2200 cm\(^{-1}\) and a
gaussian band having a long tail on low − frequency side. The nature of transition range is found to fit an allowed direct transition (Figure 4b) with the absorption fitting as \( A_hv = B \left( hν − E_g \right)^{\frac{1}{2}} \). However, this shows amorphous or strongly disordered nature of the sample. The gaussian band is also fitted by \( \ln A \) vs \((K − K_0)^2\) which is found to be a straight line (Figure 4c).

The FTIR spectrum of DDQ complex of BEDT – TTF shown in (Figure 5a) consists of a nature of interband transition between 2800 cm\(^{-1}\) and 1800 cm\(^{-1}\) and a gaussian band around 1346 cm\(^{-1}\). The analysis of nature of transition is carried out by finding \( A_hv = B \left( hν − E_g \right)^{\frac{1}{2}} \) as the best fit (Figure 5b) which is an allowed direct transition in a disordered material. The gaussian band is also fitted (Figure 5c) showing the delocalization of charge carriers.

The FTIR spectrum of Chloranil complex of BEDT – TTF is shown (Figure 6a). It also contains a range of interband transition below 2800 cm\(^{-1}\) gaussian

Band around 1240 cm\(^{-1}\). The nature of transition is also again an allowed direct type (Figure 6b) and a weak gaussian is also fitted (Figure 6c). The gaussian band is weaker as compared to gaussian band in the case of DDQ complex.

Finally, the FTIR spectrum of iodine complex of BEDT – TTF is shown (Figure 7a). This spectrum consists of a half − power beta density from 3800 cm\(^{-1}\) to 1500 cm\(^{-1}\) and a triangular distribution below 1500 cm\(^{-1}\). The half − power beta density is fitted (Figure 7b), which shows hopping transport in the layers of BEDT –TTF.

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molecules is enhanced by iodine molecules and I$_3^-$ ions. The triangular distribution below 1500 cm$^{-1}$ reveals imperfect nesting or screening of charge carriers. Such a distribution is found among ternary charge transfer complexes having two donors and one acceptor (25). So, this can be related to neutral BEDT – TTF molecules and ionic BEDT – TTF$^+$ serving as two donors.

4. Conclusions:

BEDT – TTF itself shows hopping conduction associated with beta density in IR range. This beta density is enhanced in BEDT – TTF – TCNQ and BEDT – TTF – I$_2$ showing hopping mechanism of conduction in these two complexes. Band conduction is observed in TCNE, DDQ, and Chloranil complexes with interband transition in IR range. These three complexes also show a gaussian distribution associated with electronic delocalization.
Figure 1 Molecular structures of BEDT – TTF and organic acceptors

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Figure 2a FTIR spectrum of BEDT – TTF

Figure 2b half – power beta density fit

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Figure 2c Gaussian band fit

Figure 3a FTIR spectrum of BEDT – TTF – TCNQ

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Figure 3b half–power density fit

Figure 4a FTIR spectrum of BEDT – TTF – TCNE

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Figure 4b Allowed direct transition with $E_g = 0.247 \text{ eV}$

Figure 4c Gaussian band fit
Figure 5a FTIR spectrum of BEDT–TTF – DDQ

Figure 5b Allowed direct transition with $E_g = 0.23$ eV

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Figure 5c Gaussian band fit

Figure 6a FTIR spectrum of BEDT –TTF – Chloranil

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Figure 6b Allowed direct transition with $E_g = 0.21$ eV

Figure 6c Gaussian band fit
Figure 7a FTIR spectrum of BEDT–TTF–Iodine

Figure 7b half power beta density fit

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