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FTIR Spectroscopy of charge transfer Complexes of 1,1,4,4 – Tetraphenyl – 1, 3 – Butadiene
1. Introduction:

TPB (1, 1, 4, 4 – tetraphenyl – 1, 3 – butadiene) is well known luminescent material (1, 2) and recently its polymorphism is studied with structural and Raman spectroscopic characterization (3). The triclinic and monoclinic structures were also found earlier (4, 5). Amplified spontaneous emission was also found in TPB (6). Stimulated emission from two different species was observed in laser action (7). Fluorescence of TPB in vacuum ultraviolet light was also observed (8). The fluorescence efficiency between 900Å and 2500 Å was found to be quite high (9). The response of TPB was found high in also the range 1800 – 3800 Å (10).

The molecular structure of TPB and other organic accepters are shown (Figure 1). In the present work, the Fourier transform infrared (FTIR) spectra are studied for the charge transfer complexes of TPB.

2. Experimental:

The luminescent material TPB was mixed with standard organic acceptors such as TCNQ (7, 7, 8, 8 – tetracyano – p – quino – dimethane), TCNE (tetracyano – p – ethylene), DDQ (2, 3 – dichloro – 5, 6 – dicyno – p – benzoquinone), Chloranil and iodine in 1:1...
molecular weight proportions. The mixtures were grinded in an agate mortar with agate pastel for half an hour till the colour deepened or changed due to the formation of charge transfer complexes. After forming CTCS, they were mixed with anhydrous spectrograde KBr powder and again grinded to form homogeneous mixtures. Then they were compressed to form round pellets were placed in the dark chamber of spectreophotometer.

The spectra in the range 400 – 4000 cm$^{-1}$ were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin Elmer Company, USA having a resolution of 0.15 cm$^{-1}$, a scan range of 15,000 – 30 cm$^{-1}$, 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 – 370 cm$^{-1}$. The spectra were recorded in purge mode.

3. Results and Discussion:

The FTIR spectrum of TPB is shown (Figure 2a). It contains a half – power beta density described by

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

where $K^{*} = (K - a)/b$ in which $a$ is the initial value of the peak and $b$ is the basewidth of the peak. It is found in the range 1700 – 3500 cm$^{-1}$ range. This flat peak is followed by a gaussian distribution
below 1700 cm\textsuperscript{-1}. The beta density and gaussian bands are fitted (Figure 2b and 2c). A U–shaped distribution is found in transmission which is related with anisotropic disorder. An isotropic distribution of disorders should give rise to a semi–circular distribution (11). This also indicates that there are two sites and probabilities of occupation of these sites are different leading to such an anisotropic disorder (12).

The FTIR spectrum of TPB – TCNQ is also shown (Figure 3a). There is a very broad transmission dip covering the complete IR–range corresponding to broad absorption peak around 1600 cm\textsuperscript{-1}. This is related with a broad peak in the imaginary part of dielectric constant because

\[
\sigma_1(\omega) = \omega E_2(\omega) / 4\pi = \alpha(\omega) n_1(\omega) c / 4\pi
\]

where \(\alpha(\omega)\) is absorption, \(n_1(\omega)\) is real part of refractive index, \(E_2(\omega)\) is the imaginary part of dielectric constant and \(\sigma_1(\omega)\) is the real part of optical conductivity. The accurate calculations if \(E_2\) and \(\sigma_1\) from this background absorption show an oscillator doublet with a small dip around 1000 cm\textsuperscript{-1} (Figure 3b and 3c). This is related with Peierls distribution of either TPB stacks or acceptor stacks as assigned in KCP –Br and TTF – TCNQ. The imaginary part of dielectric constant shows a peak since dielectric constant of a Peierls distributed lattice is high because of metallic segments embedded in a dielectric medium. The optical conductivity shows a peak because of its increase by a borrowing an oscillator strength from dc conduction.
which decreases. The oscillator towards the low frequency side than 1000 cm$^{-1}$ is like a gaussian band. The higher frequency oscillator is highly damped oscillator because only heavily – damped oscillator leads to gaussian distribution.

The FTIR spectrum of TPB – TCNE shown (Figure 4a) also contains broad background absorption around 1500 cm$^{-1}$. Here also the imaginary part of dielectric constant is calculated and a curve is found which can be deconvoluted. The deconvolution leads a low frequency oscillator around 1200 cm$^{-1}$ and a Cauchy distribution around 2000 cm$^{-1}$. The Cauchy distribution is an approximation of gaussian band as follows. The gaussian function described by

$$\alpha = \alpha_0 \exp\left[-\frac{(K - K_0)^2}{2M^2}\right]$$

can be approximated for large $M^2$ as

$$\alpha \cong \alpha_0 \left[ 1 - \frac{(K - K_0)^2}{2M^2} \right]$$

$$\alpha \cong \frac{\alpha_0}{1 + \frac{(K - K_0)^2}{2M^2}}$$

This Cauchy distribution around $K_0$ for large damping coefficient. The Cauchy distribution is associated with almost free charge carriers and delocalization is more pronounced as compared to the gaussian distribution. The imaginary part of dielectric constant and real part of optical conductivity are plotted (Figure 4b and 4c) which may be deconvoluted as above.
The FTIR spectrum of TPB – DDQ is shown (Figure 5a). This spectrum contains a range between 3000 cm\(^{-1}\) and 1800 cm\(^{-1}\) where the absorption is constant. This is indicative of the fact that TPB – DDQ is a layered or two-dimensional material. The other range is a gaussian band around 1400 cm\(^{-1}\). This gaussian is fitted (Figure 5b) showing the electronic delocalization.

The FTIR spectrum of TPB – Chloranil (Figure 6a) is different from those of other complexes. This spectrum contains a range of nature of interband transition between 2800 cm\(^{-1}\) and 1700 cm\(^{-1}\). The absorption is analyzed as (Figure 6b)

\[ A h \nu = B (h \nu - E_g)^{1/2} \]

which is a function for an allowed direct transition. Thus TPB – Chloranil is a semiconductor. Below 1600 cm\(^{-1}\), there are three repetitions of a structure associated with square singularity along a homomolecular sublattice of Chloranil stacks. There are oscillations in the density of states.

The spectrum of TPB – iodine in IR range (Figure 7a) again contains a range of double oscillator model. The lower frequency oscillator is around 400 cm\(^{-1}\). The higher frequency oscillator around 1000 cm\(^{-1}\) is almost a gaussian distribution due to large damping coefficient (Figure 7b and 7c).
4. Conclusions:

It shows hopping conduction in infrared range. TPB – TCNQ shows a double oscillator model with high frequency oscillator showing gaussian band. TPB – TCNE also shows a double oscillator with high frequency oscillator as a Cauchy distribution. This shows validity of Drude model for metal in the case of TPB – TCNE. TPB – DDQ is found to be a two – dimensional semiconductor. TPB – Chloranil shows usual interband transition for a semiconductor and oscillations in the density of states. TPB – I\(_2\) is again similar to TPB – TCNQ.
Figure 1 Molecular structure of TPB and organic acceptors

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Figure 2a FTIR Spectrum of TPB

Figure 2b half – power beta density fitted

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Figure 2c Gaussian band fit

Figure 3a FTIR spectrum of TPB – TCNQ

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Figure 3b Imaginary part of dielectric constant in IR range

Figure 3c Real part of optical conductivity in IR range
Figure 4a FTIR spectrum of TPB – TCNE

Figure 4b Imaginary part of dielectric constant in IR range

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Figure 4c Real part of optical conductivity in IR range

Figure 5a FTIR spectrum of TPB – DDQ

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Figure 5b Gaussian band fit

Figure 6a FTIR spectrum of TPB – Chloranil

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Figure 6b Allowed direct transition fitted with $E_g = 0.22$ eV

Figure 7a FTIR spectrum of TPB – Iodine
Figure 7b Imaginary part of dielectric constant in IR range

Figure 7c Real part of optical conductivity in IR range

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References:


