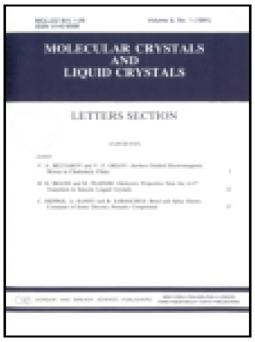

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Infrared Spectroscopy of Charge Transfer Complexes of D-Luciferin

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D-luciferin, the luminescent material of firefly, forms charge transfer complexes with organic acceptors such as TCNQ, TCNE, chloranil, DDQ, and iodine. The infrared spectra reveal indirect allowed transition across a single particle gap in the IR range and guassian background absorption. TCNE complex shows triangular distribution due to imperfect nesting. Chloranil complex shows oscillations in the density of states without much dampingthe.

Keywords D-luciferin; innfrared spectroscopy; gaussian distribution; nature of transition

1. Introduction

Organic charge transfer complexes are found to be semiconductors [1, 2, 3]. Orgenosulfur chemistry plays important role due to highly dipolar C–S bond. Luciferin, lightemitting biological pigment leading to biolu-minescence, contains two C–S bonds which have large dipole moments. Also luciferin has C–C bridge structure like TTF. There are special C–H and C-COOH bonds which also make luciferin dipolar and flexible. Light emitting molecule is utilized by luciferage or photoprotein [4, 5]. Luciferins are oxidized in the presence of the enzyme luciferage to produce oxyluciferin and energy in the form of light [6]. Firefly luciferin emitting yellow light with the help of ATP. [7, 8]· In the present study, the FTIR spectra of luciferin and its charge transfer complexes with organic acceptors such as TCNQ, TCNE, DDQ, chloranil, and iodine have been studied.

1.1. Results and Discussion

The luciferin molecule contains a C–C bridge and two C–S bonds. Special bonds of C–H and C-COOH are also shown. There is a mechanical strain generated due to special bonds which are equivalent to the availability of polar optical phonons associated with the additional molecular flexibility.

The FTIR spectrum of luciferin is shown in Fig. 1.

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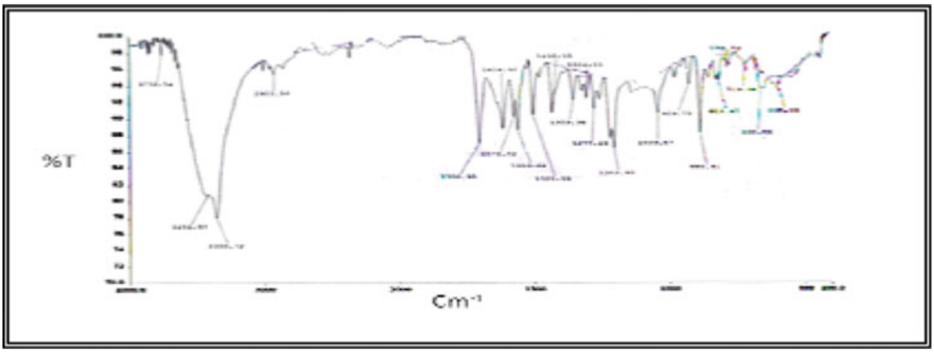

Figure 1. The FTIR spectra of luciferin.

The stacks of luciferin conduct electricity and luciferin is a semiconductor. This is revealed by a nature of transition observed in the range of 1800 cm^{-1} to 3100 cm^{-1} as dhoen in Fig. 2.

An indirect transition is concluded on the basis of $\alpha h\nu = \alpha_0(h\nu - E_g \pm E_p)^2$ type behavior of transition. The indirect transition rather than a direct transition is because of polar optical phonons associated with special bonding although luciferin is a small molecule and not a macromolecule. This is similar to stress due to hydrogen bonding in quin hydrone. [9] The noise observed above 3500 cm^{-1} reveals photo conducting nature of luciferin. Below 1800 cm^{-1}, a broad background gaussian distribution in absorption is observed. This gaussian has been fitted as Fig. 3.

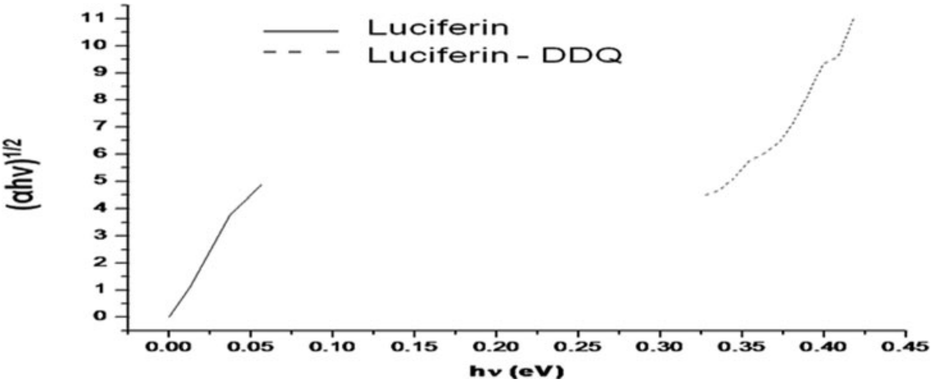

Figure 2. Analysis of allowed indirect transition in luciferin and luciferin-DDQ.

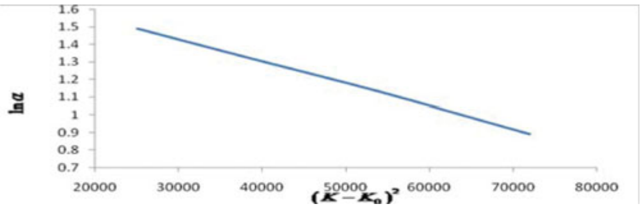

Figure 3. Analysis of background gaussian absorption in luciferin.

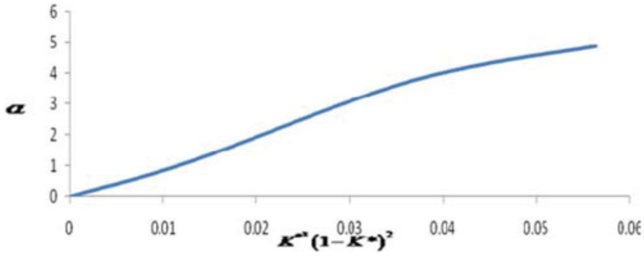

Figure 4. Low-frequency square power beta density in luciferin.

Finally, below 700 cm^{-1}, a square power beta density is observed obeying $\alpha = \alpha_0 K^{*2}(1 - K^*)^2$. The presence of this beta density reveals the presence of low-frequency hopping process which is fitted as shown in Fig. 4.

The FTIR spectrum of luciferin-TCNE is shown in Fig. 5.

There is imperfect nesting in this compound as proposed theoretically in other compounds [10]. This leads to two almost triangular distributions which are asymmetric triangular distributions can also be observed when there are triangular rather than rectangular potential barriers are present [11]. In this case, there is tunneling of charge carriers through a triangular potential barrier. The probability of tunneling is enhanced by three orders of magnitude as compared to tunneling through a rectangular potential barrier. The nature of transition in the range 1800–2900 cm^{-1} is analyzed and it is found that absorption α obeys $\alpha h\nu = \alpha_0(h\nu - E_g \pm E_p)^2$ corresponding to allowed indirect transition as shown in Fig. 6.

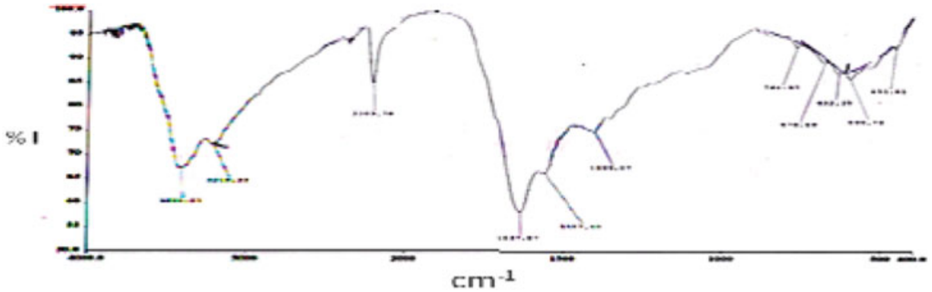

Figure 5. The FTIR spectrum of luciferin-TCNE.

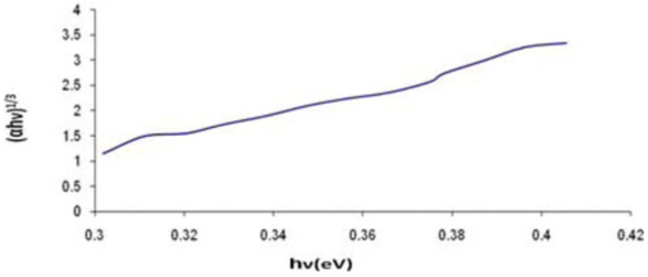

Figure 6. Analysis of allowed indirect transition in luciferin-TCNE.

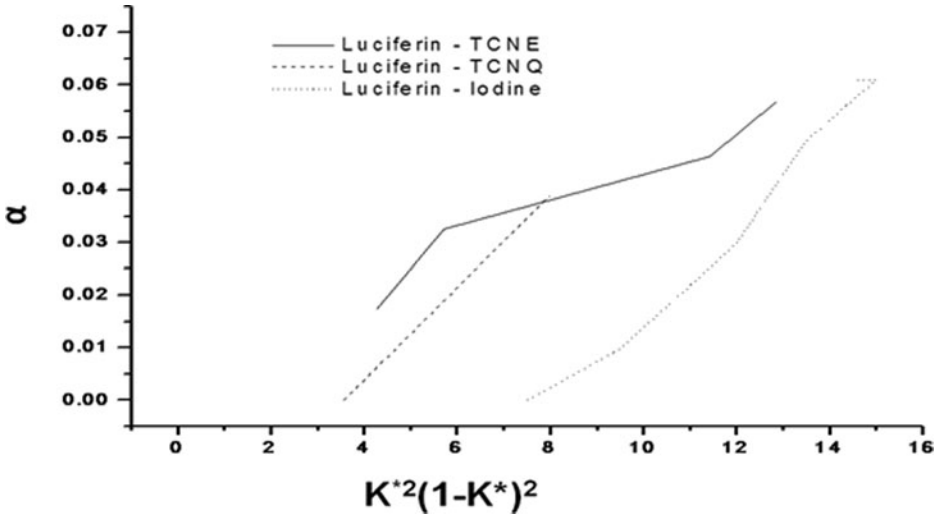

Figure 7. Low-frequency square-power beta density in luciferin-TCNE, luciferin- TCNQ, and luciferin-iodine.

Charge transfer complexes of small donor and acceptor molecules usually show direct transition [12]. However, when polar optical phonon is involved, it may show indirect transition [13]. Even hydrogen bonding leads to indirect transitions [9]. Here indirect transition is observed because of unusual or unconventional C–H and C-COOH bonds in luciferin. Finally, a square power beta density obeying $\alpha = \alpha_0\ (1-K^*)^2$, where $K^{*2} = K-a/b$ is observed in the spectrum of luciferin-TCNE below 700 cm^{-1} associated with low-frequency hopping process is shown in Fig. 7.

This corresponds to Bernoulli trials in hopping mechanism in an ionic material either hops due to photon-assistance or does not hop due to coulomb repulsion and localization effects. Charge carriers are coupled with rocking, waggins and twisting vibrations rather than getting coupled with stretching and deformation vibrations at low enough frequencies.

The infrared spectrum of luciferin-TCNQ is shown in Fig. 8. The nature of transition is observed in the range of 1800–3200 cm^{-1} again an allowed indirect transition as concluded on the basis of analysis as in Fig. 9.

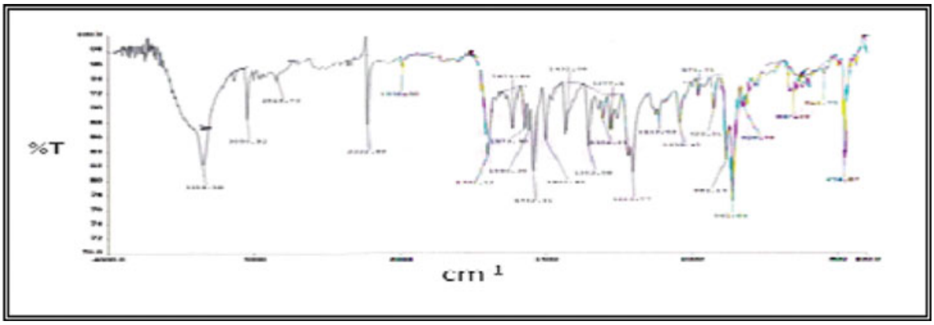

Figure 8. The FTIR spectrum of luciferin-TCNQ.

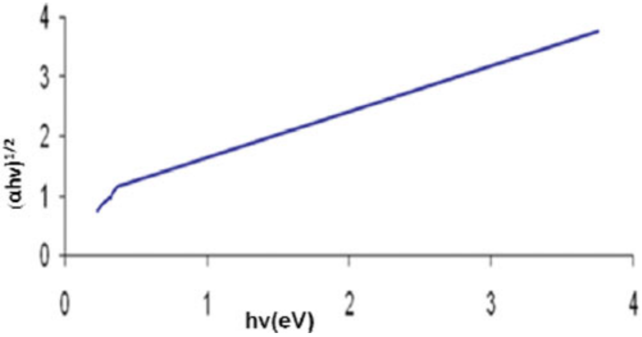

Figure 9. Analysis of allowed indirect transition in luciferin-TCNQ.

Gaussian around 1400 cm^{-1} is sufficiently enhanced compared to the spectrum of only luciferin. This reveals more conducting nature of TCNQ complex. Finally, a square power beta density which is quite asymmetric below 700 cm^{-1} is analyzed in Fig. 7.

The interpretation of gaussian and beta density remain the same as discussed above. Gaussian line-shape rather than lorentzian line shape for the envelope shows nonionic nature of the complex. Fully ionic complex will show oscillator model fitting lorentzian rather than Gaussian distribution and spectra will be governed by acceptor vibrations. Here the spectrums of luciferin govern the spectrum of charge transfer complex. Also gaussian distribution shows absence of electron–phonon resonance from Fig. 10.

Incommensurate nature of charge density wave is also supported by gaussian band. This is related with delocalization of charge carriers in a small band gap semiconductor. Metallic nature should lead to broadening of gaussian band ultimately resulting into Cauchy distribution satisfied by the Drude model. Thus gaussian line-shape is first step towards suppression of Peierls transition in a one-dimensional conductor.

The FTIR spectrum of luciferin-DDQ is also shown in Fig. 11. Here also nature of transition is an allowed indirect type showing two or three thresholds due to phonon energy.

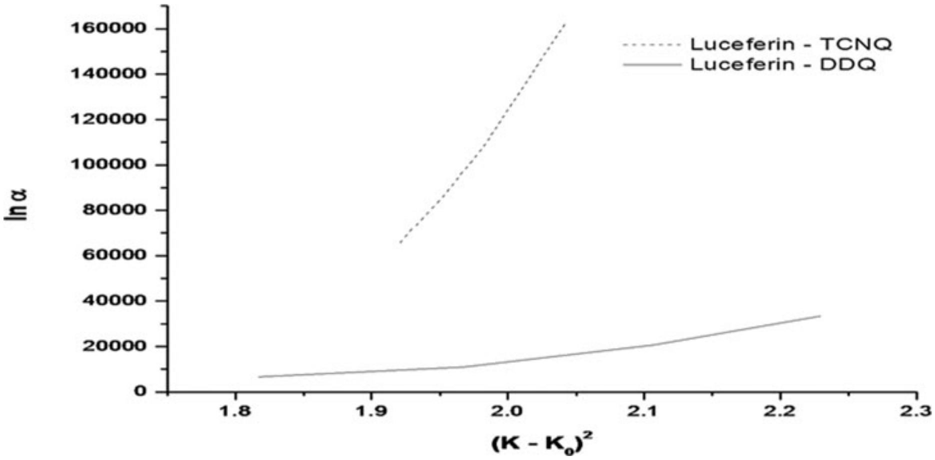

Figure 10. Analysis of background gaussian absorption in luciferin-TCNQ and luciferin-DDQ.

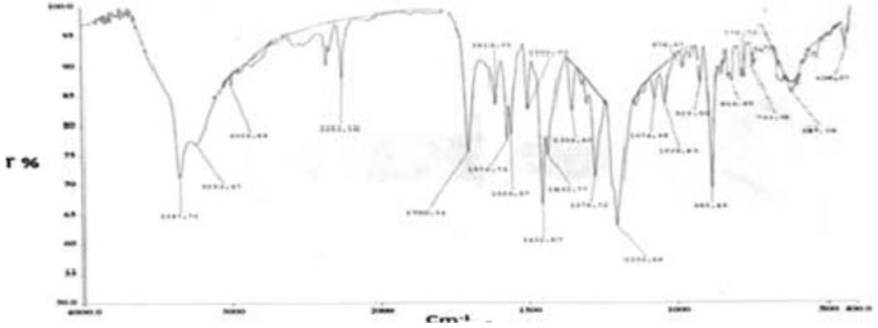

Figure 11. The FTIR spectrum of luciferin-DDQ.

A phonon-assisted transition occurs around a single particle gap. A broad and intense Gaussian band is observed which is analyzed in Fig. 10.

The FTIR spectrum of luciferin–chloranil shows completely different features is shown in Fig. 12.

In the present case, a nature of transition is observed which is indirect forbidden type obeying $\alpha h\nu = \alpha_0(h\nu - E_g \pm E_p)^3$ and fitted as shown in Fig. 13.

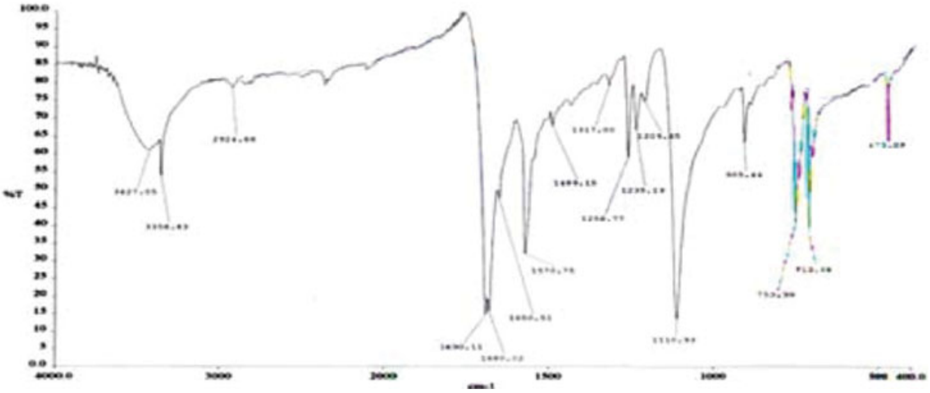

Figure 12. The FTIR spectrum of Luciferin-Chloranil.

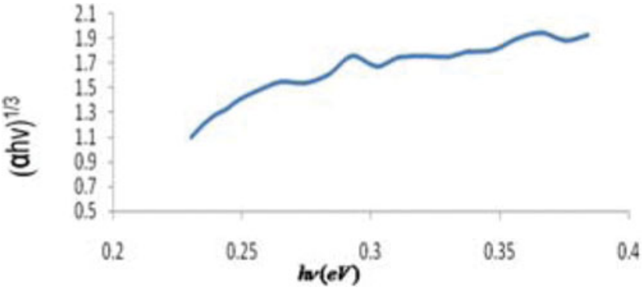

Figure 13. Analysis of forbidden indirect transition in luciferin-chloranil

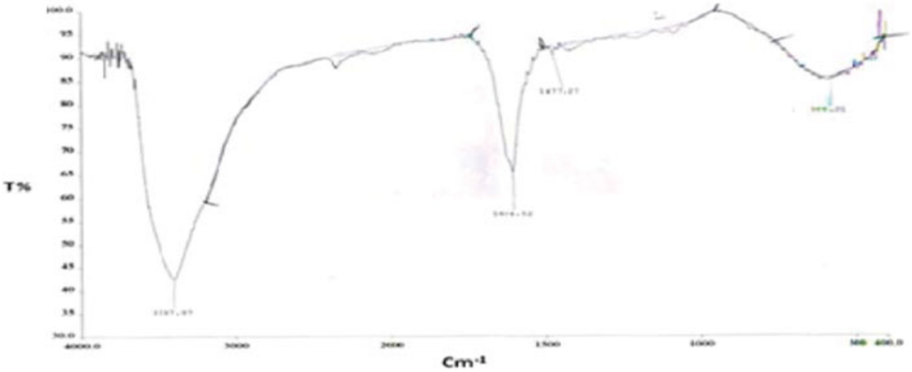

Figure 14. Figure 3.18: The FTIR spectrum of luciferin-iodine.

The transition becomes forbidden in this case because of larger intermolecular distances as observed in β and γ-cyclo dextrins–iodine complexes [14]. Apart from this change in nature of transition, there are repetitions of structures without any dampings are found below 1700 cm^{-1}. This can be attributed to the oscillations in the density of states of phonons also found in biocytin–chloranil complex. The charge transfer be used as molecular multivibrators as in the case of some of the acrodine orange complexes [15]. There are three repetitions with reducing width only at low frequencies in the transmission without much change in maximum transmission. The transverse optical phonons get coupled with charge carriers and give rise to similar effect as observed in the presence of magnetic field. Square-root singularity in one-dimension leads to exact interpretation of the shapes of repeated structures. The density of states shows repeated divergences at particular frequency.

The last is the spectrum of luciferin-iodine is shown in Fig. 14.

It is also shows an allowed indirect transition similar to the one observed in other CT complexes of luciferin with organic acceptors as shown in Fig. 15. A square-power beta density observed below 700 cm^{-1} is also analyzed as in Fig. 16.

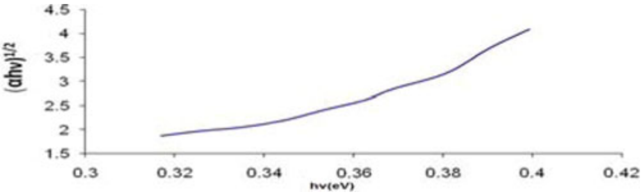

Figure 15. Analysis of allowed indirect transition in luciferin-iodine.

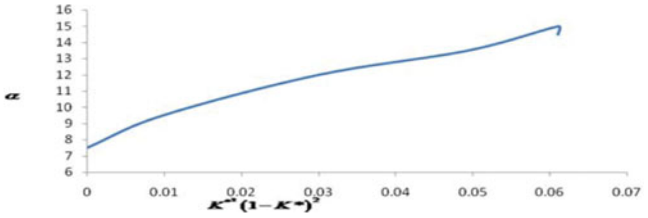

Figure 16. low-frequency square-power beta density in luciferin-iodine.

Table 1. Band gaps and phonon energies in CT complexes of luciferin

Sr. No.	Name of Complex	Indirect band gap E_g(eV)	Phonon energy E_p(eV)
1	Luciferin	0.23	0.06
2	Luciferin-TCNE	0.26	0.02
3	Luciferin-TCNQ	—	—
4	Luciferin-DDQ	0.34	$E_{i1} = 0.02$ $E_{i2} = 0.07$
5	Luciferin-Iodine	0.29	0.027

Table 2. Width of Gaussian and beta density background envelops

Sr. No.	Name of complex	FWHM (cm^{-1}) of Gaussian bands	FWHM (cm^{-1}) of beta density
1	Luciferin	559.524	226.19
2	Luciferin-TCNE	—	307.31
3	Luciferin-TCNQ	829.22	207.31
4	Luciferin-DDQ	731.71	—
5	Luciferin-Iodine	—	280.49
6	Luciferin-Chloranil	—	—

The value of forbidden energy gaps and phonon energy of phonons involved in indirect gaps are evaluated from analysis and are tabulated in Table 1. The full width at half-maximum of the gaussian as well as square-power beta density are also tabulated for luciferin and its CT complexes in Table 2.

2. Conclusion

The infrared spectra of D-luciferin and its CT complexes reveal allowed indirect transition across a single-particle band gap lying in the mid-IR range. A gaussian distribution almost always observed except in chloranil complex indicates delocalization effects governing small band gap semiconducting nature. TCNE complex reveals imperfect nesting and chloranil complex reveals nesting and oscillations in the density of phonon states.

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