RESEARCH ARTICLE

VIBRATIONAL SPECTRA OF TERNARY CHARGE TRANSFER COMPLEXES OF PYRENE

Patel A.N[1*]., Solanki G.K.[2] and Oza A.T [2]

[1]Sheth M.N. Science College, Patan-384 265, Gujarat, India
[2]Department of Physics, Sardar Patel University, Vallabh Vidyanagar- 388 120, Gujarat, India

A R T I C L E   I N F O

A B S T R A C T

Pyrene, a condensed hydrocarbon forms ternary CTCs with chloranil – I_2, DDQ – I_2, TCNQ – I_2 and TCNE – I_2 combinations. The FTIR spectra of these ternary complexes have been studied. They show forbidden direct transitions in three ternary complexes except TCNQ complex in which it is allowed direct transition. Only chloranil and DDQ complexes show band gap at 0.1125 eV ($E_P/2$). However, actual absorption show exciton bands in these excitonic semiconductors. There is a possibility of electron-exciton interaction in these ternary complexes of pyrene, which can be called exciplexes.

INTRODUCTION

A very few studies on the ternary charge transfer complexes which are either metallic or semiconducting have been available [1 to 7]. Recent advances in the subject of ternary complexes has even led to superconducting phase at low temperatures in both two donors and one acceptor [8-14] and one donor and two acceptor types of such complexes [15-21]. Pressure effects and magnetic field effects on the transport properties on some other strongly correlated electronic systems have also been studied [22, 23]. The possibility of Frohlich superconduction in high magnetic field has been explored [24]. Theory for unconventional density waves is also developed [25, 26].

In the present work we have reported the ternary CT complexes based on pyrene as a donor. The four complexes namely pyrene-chloranil-I_2, pyrene-DDQ-I_2, pyrene-TCNQ-I_2 and pyrene-TCNE-I_2 show the infrared spectra different from those of the ternary conductor based on TMPD, DPPD and benzidine because of π-conjugated network instead of local charge transfer resulting in ionization or quaternization due to local charge transfer.

Experimental

Pyrene, the condensed aromatic hydrocarbon having four rings symmetrically arranged, formed blue CT complex with iodine in 1:1 proportion. This binary CT complex was converted into the ternary complexes namely pyrene-chloranil-I_2, pyrene-DDQ-I_2, pyrene-TCNQ-I_2 and pyrene-TCNE-I_2 by adding and grinding with the well-known organic acceptors namely chloranil, DDQ (2,3- dichloro-5,6-dicyano-p-benzoquinone), TCNQ (7,7,8,8-tetracyano-p-quinodimethene) and TCNE (N,N,N′,N′,-tetracyanoethylene).

The infrared spectra were recorded in 400-4000 cm^{-1} range by the Perkin-Elmer spectrophotometer. For this, samples were prepared as circular discs with a compressor and die operated manually after dispersing a small amount of ternary complex in a large amount of dry spectrograde KBr powder.

The infrared spectra as recorded are shown in Figure 1 (a-d). These spectra were found to be different from those of its separate constituents as well as those of the binary subsystems.

RESULTS AND DISCUSSION

In the cases of recently studied ternary CT complexes of donors such as benzidine, TMPD and DPPD, a two-conduction band model leads to two absorption edges [27-29] This is not the case here where the donor has π-conjugated network. The main absorption edge revealing a band gap of about 0.225 eV can be associated with the Peierls gap found even in binary charge transfer complexes. It remains a direct transition from the valence band of donor to the conduction band of organic acceptor. The infrared spectra of the four complexes, are shown [Figure1 (a-d)].

The spectra of pyrene-CA-I_2 and pyrene-DDQ-I_2 are divided in five parts:

➤ Between 4000cm^{-1} and 2800cm^{-1} where a broad and intense band has been observed. This is modified differently in the ternary complexes of different organic acceptors. This band is more pronounced and broader in the DDQ complex than in the chloranil complex.
➤ The second range (1750-2800cm^{-1}) belongs to the absorption due to transition between the valence and conduction band (the upper conduction band) and the nature of transitions are analyzed [Figure.2 (a-d)]. It is a direct transition obeying

$$\alpha h\nu = A\,(h\nu\text{-}Eg)^{3/2}$$

Indicating forbidden transition in the three pyrene ternary complexes except the fourth TCNQ based complex which reveal $\alpha h\nu = A\,(h\nu\text{-}Eg)^{1/2}$ associated with an allowed direct transition. As far as this upper absorption edge is concerned this transition is similar to the one existing in the binary CT complexes.
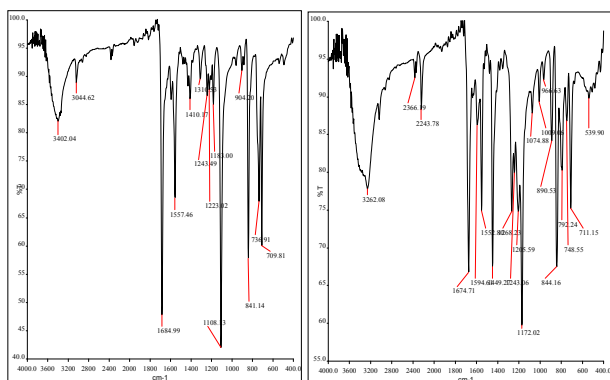

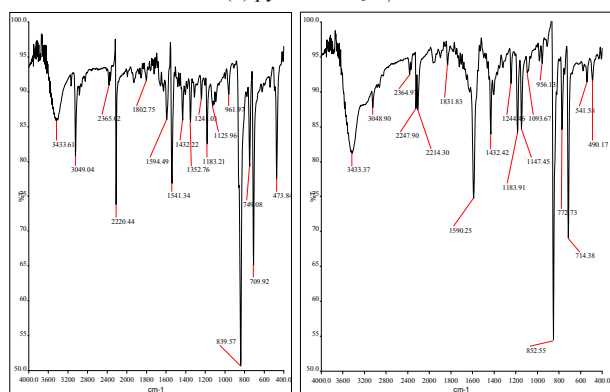**Figure 1** Infrared spectra of (a) pyrene-chloranil-I$_2$, (b) pyrene-DDQ-I$_2$,

Figure 1 Infrared spectra of (c) pyrene-TCNQ-I$_2$ and (d) pyrene-TCNE-I$_2$
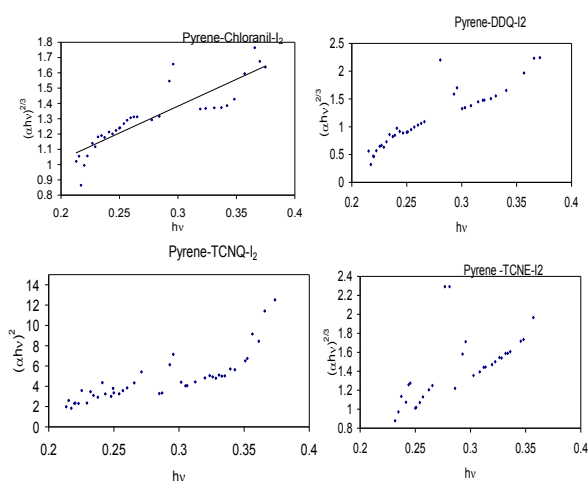

Figure 2 Analysis of direct band gaps (a) pyrene-chloranil-I$_2$, (b) pyrene-DDQ-I$_2$, (c) pyrene-TCNQ-I$_2$ and (d) pyrene-TCNE-I$_2$

Moreover, there is additional shrinkage due to electron-electron scattering which is non-universal, i.e. it differs from each other when organic acceptors are changed. When inter-molecular distance is small in TCNQ complex the allowed rather than forbidden direct transition is found as well as band gap is reduced to 0.205 eV, i.e. the shrinkage $\Delta_1 = 0.020$ eV is

large. This shows there is more electron-electron scattering due to reduced inter-molecular distance.

The direct excitations in the direct Peierls gap are verified as sharp peaks in absorption in the band gap region (Figure 2). The excitation bands exist at 0.365 eV and 0.30 eV in the three complexes except the TCNQ complex in which one more low-lying exciton band is found at 0.275 eV. Excitations exist in direct band gap semiconductors which is bound electron-hole pairs in a non-degenerate semiconductors like the four ternary complexes or pyrene. The π-cloud delocalization of electrons on pyrene molecule over four benzene rings is not sufficient to suppress the Peierls gap. In ternary complexes of perylene, both of single-particle gap and double particle gap are replaced by Gaussian distributions due to Gaussian density of states within the forbidden energy gap and the gaps are smeared out by free-carrier absorption, due to π-cloud delocalization over five rings. The perylene complexes are almost metallic.

> The third part (1200-1800cm^{-1}) is a transmitting range where absorption is negligible and there is large number of sharp bands due to the intramolecular vibrations. The absence of resonance-antiresonance spikes observed in strongly interacting donors and acceptors in radical-ion salts reveal that there is no stabilization of the middle conduction band having large band-width. Neither the bands (valence band and lower conduction band) are coupled through any Gaussian absorption nor the free-carrier absorption occurs in the conduction band.

> This short-range, 800-1000 cm^{-1} is associated with transition observed in the ternary complexes with local charge transfer. The four-ring delocalization of π-cloud in pyrene is not sufficient to couple the bands with any Gaussian absorption. Rather the nature of transition is analyzed [Figure 3(a –b)].
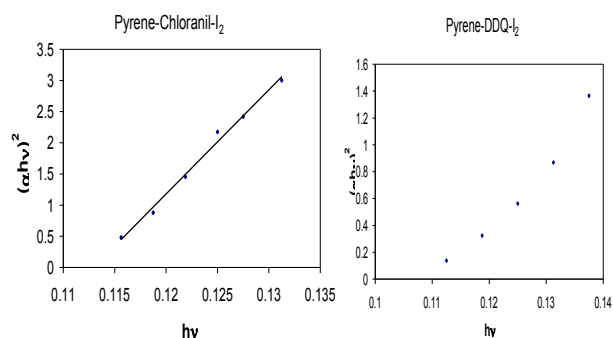

Figurer 3 Analysis of the lower absorption edge for (a) pyrene-chloranil-I$_2$ and (b) pyrene-DDQ-I$_2$ which indicates, allowed direct transitions

It is a two-particle gap ($E_P/2 = 0.1125$ eV), i.e. both of electron and hole are free carriers. However, transition is direct rather than indirect showing two conduction bands with associated band edge at K=0.

> This part is the lowest in wave numbers i.e. 400-800cm^{-1}, and the spectra indicate Gaussian absorption related with delocalization of charge cloud in the CT complexes [Figure 4(a-b)].
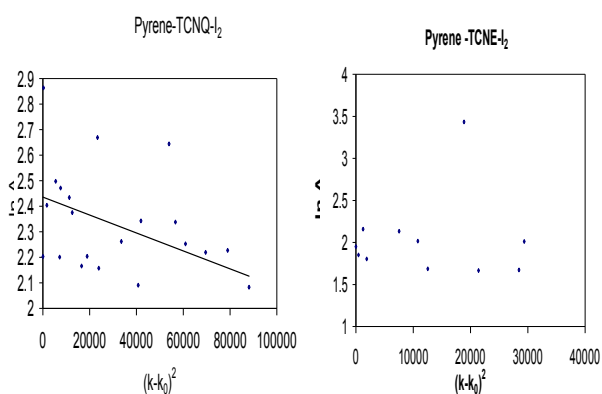
1113

Figure 4 Lower energy Gaussian distributions fitted for
(a) pyrene-TCNQ-I_2 and (b) pyrene-TCNE-I_2

The spectra of pyrene-TCNQ-I_2 and pyrene-TCNE-I_2 show direct transitions when analyzed for the upper optical absorption edge similar to the chloranil and DDQ complexes. These spectra differ in the third and fourth ranges (900-1600 cm^{-1}) which merge due to a Gaussian absorption analyzed [Figure 5 (a-d)] rather than a clear lower absorption edge. This is related with delocalized π-cloud over four rings in pyrene giving rise to more charge transfer to TCNQ and TCNE with cyano groups than the DDQ and chloranil having not all cyano groups and only (all four) chlorine ions, respectively.
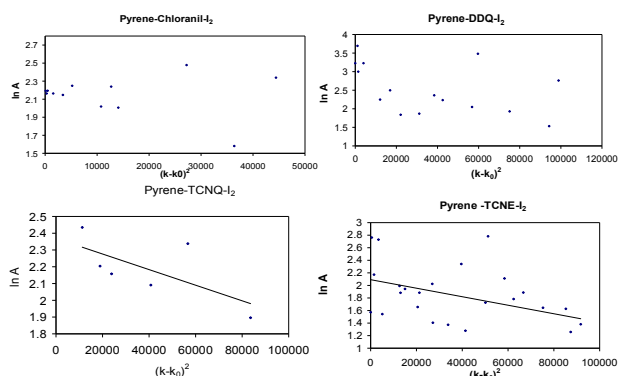

Figurer 5 Gaussian distributions fitted for (a) pyrene-chloranil-I_2, (b) pyrene-DDQ-I_2, (c) pyrene-TCNQ-I_2 and (d) pyrene-TCNE-I_2

There can be two conduction band model applicable in a semiconductor (30) whether it is inorganic or ternary organic compound. The pyrene ternary compounds studied in the present work also reveal two-band transport particularly in the chloranil and DDQ complexes. In TCNQ and TCNE complexes, the lower absorption edge is not clear because of a Gaussian absorption in the gap region. It is possible that it is related with the Madelung constant or the electrostatic binding energy following a Gaussian distribution in the momentum with the width determined by an arbitrary point [31]. This particularly happens when ionic sub-lattices are present.

The heavily-doped semiconductors follow Burstein-Moss shift (high frequency shift of the band gap due to band-filling effects) which is not observed. Incommensurate-to-commensurate transition is possible only if charge density waves are formed. Low values of maximum absorption discard this possibility. The order-disorder transition present in alloys (inorganic or organic) is also absent.

There is possibility of neutral-to-ionic transition in the formation of a ternary complex from a binary complex. Thus the ternary CT complexes may behave like a complex (2:3 or 1:2) binary salts in the place of simple (1:1) salts. There can be competitive and cooperative binding of two acceptor molecules with one organic donor.

This may lead to disorder. Benzidine, DPPD and TMPD based ternary CT complexes where charge transfer is localized do lead to disorder in the molecular packing. Here in the π- delocalized pyrene and perylene complexes, disorder as revealed through band tailing is not observed. The band structure of ternary CT complexes may be also explained by bonding, non-bonding and anti-bonding orbitals with the weaker acceptor leading to non-bonding orbitals after hybridization. There may be two charge transfer bands present in the ultraviolet-visible spectra because of two acceptors having non-degenerate coupling with donor.

The presence of two Gaussian distributions rather than two-oscillator model indicates electronic delocalization and heavily-damped oscillatory behaviour. The absence of free-carrier absorption in any range of the mid-IR spectra reveals narrow conduction bands limiting the mobility. The absence of band-tailing or tunneling leading to Franz-Keldysh effect arising from internal electric field reveal absence of localization within the band gap. There is presence of noise near the upper band gap associated with the non-degenerate localized states due to only partial stabilization of the conduction band.

There exist electron-exciton interaction between electrons at the Fermi level at the middle of the Peierls gap and excitons because of coupling between electrons and holes in the conduction and valence bands. Such complexes are called "exciplexes". The electrons at the Fermi level are repelled by electrons in conduction band and are attracted by holes in the valence band. As a result, the Fermi level goes down towards the valence band.

There is possibility of electron-exciton interaction because of the Fermi level stabilized by one of the acceptor molecules lying in the gap region of the larger band gap. The electron-hole pair created across the larger gap (about 0.22eV) can interact with the electrons or holes donated by the additional acceptor molecules. The details of infrared absorption edges and Gaussian envelopes are summarized in Tables 1 & 2

Table 1 Infrared absorption edge for ternary CT complexes of pyrene

Name of the complex	Upper absorption edge			
	Absorption function	Nature of transition	Band gap (E_g)	Shrinkage (meV)
Pyrene-chloranil-I_2	$\alpha h\nu = A(h\nu - E_g)^{3/2}$	Forbidden direct	0.217	$\Delta_1 = 8.0$
Pyrene -DDQ-I_2	$\alpha h\nu = A(h\nu - E_g)^{3/2}$	Forbidden direct	0.22	$\Delta_1 = 5.0$
Pyrene -TCNQ-I_2	$\alpha h\nu = A(h\nu - E_g)^{1/2}$	Allowed direct	0.205	$\Delta_1 = 20.0$
Pyrene -TCNE-I_2	$\alpha h\nu = A(h\nu - E_g)^{3/2}$	Forbidden direct	0.23	$\Delta_1 = 5.1$
Pyrene -DDQ-I_2	$\alpha h\nu = A(h\nu - E_g)^{1/2}$	Allowed direct	0.111	$\Delta_0 = 1.5$

Table 2 Parameters of Gaussian distributions in IR range for the ternary CT complexes of pyrene

Name of the complex	Upper Gaussian				Lower Gaussian			
	Central wave-number K_0(cm^{-1})	Maximum absorption %	Base width (cm^{-1})	Shrinkage (meV) Δ	Central wave-number K_0(cm^{-1})	Maximum absorption %	Base width (cm^{-1})	Shrinkage (meV) Δ
Pyrene-chloranil-I_2	1350 (0.168 eV)	6%	700	57	-	-	-	-
Pyrene-DDQ-I_2	1400(0.175 eV)	4%	800	50	-	-	-	-
Pyrene-TCNQ-I_2	1300(0.162 eV)	8%	800	63	650(0.0813 eV)	7%	500	31.2
Pyrene-TCNE-I_2	1300(0.162 eV)	4%	850	63	550(0.0687 eV)	6%	600	43.8

Table 3 Exciton bands in ternary CTCs of pyrene

Name of the complex	Exciton band energy (eV)	Quantum numbers (n)
Pyrene-chloranil-I_2	0.360	1
	0.300	2
	0.270	3
	0.230	4
Pyrene-DDQ-I_2	0.360	1
	0.285	2
	0.240	3
	0.225	4
Pyrene-TCNQ-I_2	0.365	1
	0.300	2
	0.270	3
	0.250	4
	0.230	5
	0.220	6
Pyrene-TCNE-I_2	0.360	1
	0.280	2
	0.250	3
	0.240	4

When one of the binary subsystems is photoconducting and when third component at ternary system is added, the two conduction bands having large band widths overlap and coalesce into each other. This increases electron-electron interaction by considerable amount. The difference between the standard universal Peierls gap (0.225 eV) and the photoconducting band gap (centre of the Gaussian band) determines the additional shrinkage (Δ) due to electron – electron interaction (Table 2). The increased electron-electron interaction is further supported by the scattering of data points in Gaussian fits (Figures 4 and 5). Such scattering of data points were also found in quinhydrane complexes of benzidine, DPPD and pipyridyl. (Figures in ref. 32). This comparison shows the binary subsystems and ternary complexes of pyrene are also photoconducting. The ternary have more photoconducting noise than binary subsystems

The energies of the exciton bands are given by the famous Rydeberg equation [33] i.e.

$$E_n = E_g - \frac{\mu e^4}{2\hbar^2 \in^2 n^2}$$

Where μ is effective mass, e- is electronic charge, $\hbar = h/2\pi$, h being Planck's constant, $\in$ is dielectric constant and n is the principle quantum number, E_g is the gap. Energy bands of

Mott-Wannier excitons are marked by quantum numbers (Figure 2).

CONCLUSION

The ternary complexes of pyrene are expected to be more electrically conducting than those based on benzidine, TMPD and DPPD like donors because of π-delocalized charge cloud in pyrene. The lower absorption edge is interrupted by the Gaussian absorption in TCNQ and TCNE complexes.

Bibliography

1. C. Coulon, S. Flandrois, .P Delhaes, C. Hauw, P. Dupis, Phys. Rev. B, 23: 2850, 1981
2. C. Coulon, P. Delhaes, J. Amiell, J. P. Monceau, L. M .Fabre, L. Giral, *J. Physique,*) 43 : 1721,1982
3. Andre Barraud, Pierre Lasieur, Annie Ruaudel-Teixier, Michel Van devyer, Thin Solid Films, 134 : 195, 1985
4. M. G. Abd El Wahed, S. Aaly, H. A. Hammad, S. M. Metwally, J. Phys. Chem. Solids, 55: 31, 1994
5. K. Kudo, M. Nagqoka, S. Kuniyoshi, H, Tanaka, Synthetic Metals, 71: 2059, 1995
6. Jeong-Woo Choi, Gun-Yung Jung, Se Young Oh, Won Hong Lee, Dong Myung Shin Thin Solid Films, 284: 285 876, 1996
7. A.T.Oza, Solid State Commun, 71: 1005, 1989
8. Y. Shimajo, T. Ishiguro, H. Yamochi, G, Saito, Synthetic Metals, 120: 751, 2001
9. N. L. Wang, H. Mori, S. Tanaka, J. Dong, B. P. Claymany, J. Phys. Condens. Matter, 13: 5463, 2001
10. N. Harrison, L. Balicas, J. S. Brooks, M, Tokumoto, Phys. Rev. B, 62: 14212, 2000
11. N. Harrison, C. H. Mielke, A. D. Christianion, J. S. Brooks, M. Tokumoto, Phys. Rev. Letters, 86: 1586, 2001
12. D. Andres, M. V. Kartsovnite, W. Biberacher, H. Weiss, E.Balthes,
13. H. Muler, N. Kulshch, Phys. Rev. B, 64: 161104, 2001
14. M. Maesato, Y. Kaga, R. Kondo, S Kagoshima, Phys. Rev. B, 64: 155104, 2001
15. M. Maesato, Y. Kaga, R. Kondo, H. Hirai, S. Kagoshima, Synthetic Metals, 120: 941, 2001
16. J. Wosnitza, H. Elsinger J. Hagel, S. Wanka, D. Schweizer, Synthetic Metals. 120: 705, 2001
17. S. Kamiya, Y. Shimojo, M. A. Tanatar, T. Ishiguro, H. Yamohi, G. Saito, Phys. Rev. B, 65: 13410, 2002
18. J. J. McGuire, T. Room, A. Pronin, T. Timusk, J. A. Sch-Wieter, M. E. Kelly, M. A. Kini, Phys. Rev. B, 64: 094503, 2001
A. Painelli, A. Girlando, A. Fortunelli, Phys. Rev. B, 64: 054509, 2001
19. M. A. Tanatar, S. Kagoshima, T. Ishiguro, H. Ito, V. S. Yefanov, V. A. Bonderenko, N. D .Kushah, E. B. Yagubskii, Phys. Rev. B, 62: 15561, 2000
20. Akane Sato, Hiroki Ahutsu, Kazuya Saito, Michio Sorai, Synthetic Metals, 120: 1035, 2001
21. K. D. Truong, S. Jandl, M. Poirier, Synthetic Metals, 130: 229, 2002
22. Reizo Kato, Naoya Tajima, Masafumi Tamura, Jun-Ichi Yamaura, Phys. Rev. B, 66: 020508, 2002
23. M. Enomoto, A. Miyazaki, T. Enoki, Synthetic Metals, 121: 1800, 2001
24. N. Harrison, C. H. Mielke, J. Singletn, J. S. Brooks, M. Tokumoto, J. Phys. Condens. Matter, 13: L389, 2001

25. Baazs Dora, Attila Virosztek, Kazumi Maki, Phys. Rev. B, 65: 155119, 2002

26. Balaza Dora, Kazumi Maki, Attila Viroztek, Phys. Rev. B, 66: 165119, 2002

27. Ashok N. Patel, G. K. Solanki, A.T. Oza, *International Journal of Current Research*, 2016 (communicated).

28. Ashok N. Patel, Parimal Trivedi, A.T.Oza *Ind. J. Phys.*, 80:1201-1207, 2006

29. Ashok N. Patel, G.K.Solanki, A.T.Oza, *International Journal of Applied Research*, 2016 (communicated).

30. William Paul in High pressure physics and chemistry, Vol. 1 Ed. R Sbradly, Academic Press, London and New York, p. 299, 1963

31. J.M.Ziman Principles of the Theory of Solids, Cambridge University press, Second Edition, p.40, 41, Chapter 2, 1972

32. Parimal Trivedi, Ashok Patel, R.G.Patel, V.A.Patel, A.T.Oza, *Ind. J. Pure & Appl. Phys.*, 43: 335, 2005

33. C.Kittle, Introduction to solid state physics, John Wiley and Sons, Inc. New York, Seventh Edition, p. 320, 2004

****