

SYNTHESIS AND CHARACTERIZATION OF THE CHARGE TRANSFER COMPLEXES POLYVINYL CARBAZOLE WITH TRINITROFLUORENONE

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ABSTRACT

Carbazole based polymers are materials of considerable scientific and industrial interest due to their attractive features, such as hole-transporting, high charge-carrier mobility, and electroluminescent properties.

Poly (N-vinyl carbazole) (PVK) is easily synthesized, soluble in common organic solvents, poly (N-vinyl carbazole)/2,4,7-trinitro-9-fluorenone (PVK/TNF) charge transfer complex is one of the best-known organic photos conducting materials for application in electrophotography. In the present research, a spectrophotometric method applied for the study of (colored charge transfer complexes) CTC of PVK with TNF reveals the formation of 1:1 (A:D) complex, the formation of CTC with PVK and TNF from the conductivity of the CT Complex. The concentration of the donor is affected when it reacts with the acceptor and that when we increase the concentration of the donor.

Keywords: Electroluminescent; PVK; Charge transfer complex; Electron donor-acceptor.

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1. INTRODUCTION

Charge-transfer (CT) complexation is of extraordinary significance in chemical reactions, biochemical and bioelectrochemical energy-transfer processes, biological systems, pharmaceutical analysis and drug-receptor binding mechanisms [1-3].

The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bands [4,5] and discussed widely by Foster [6]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes (CTC) in which absorb radiation in the visible region [7]. Charge transfer complexes are currently of great importance since these materials can be utilized as organic semiconductors [8,9], optoelectronic devices [10], in Organic-Inorganic Hybrid Blends for Photovoltaic Applications [11], in Organic Donor-Acceptor Solar Cells [12], as Biocompatible organic charge transfer complex nanoparticles [13], in Spectrophotometric Microdetermination of Some Drugs [14]. CT complexes are structurally well-defined systems consisting of acceptor molecules, characterized by having high electron affinities and donor molecules, characterized by having low ionization potentials [15]. CT-compounds are also very interesting materials for optical or optoelectronic applications in the NIR range, IR photodetectors as the charge transfer of tetrathiafulvalen-7,7,8,8-tetracyanoquinadimethane (TTF-TCNQ) [16]. The formation of electron donor-acceptor complexes is readily apparent from the observation of new optical absorptions when electron donors (D) are mixed with electron acceptors (A) [17].

Formation of charge transfer complexes (CTC) is based on the interaction of energetically high lying HOMO of the donor with a low energy LUMO of the acceptor. CT complexes, which exhibit interesting optical, electrical and photoelectrical properties, play an important role in many electro physical and optical processes [18]. Carbazole derivatives have been successfully incorporated in efficient photorefractive [19,20] electroluminescent [21,22].and photovoltaic devices [23,24], and organic photovoltaic devices [25]. Their good charge transport properties, many of these compounds are blue-emitting materials and can be used as energy donor in blends with other conjugated organic molecules [26,27]. Carbazole molecules have been intensively studied and still show great promise for technological applications in

optoelectronics, mainly due to their photoconductive properties. Polymers with a carbazole group such as poly (N-vinyl carbazole) (PVK) have been widely used as photoconductive layers in xerographic industry, memory device and potentially solar cells [27]. PVK is also used as host polymer for hole-transporting molecules in OLED to enhance the native hole-transporting properties [28]. Poly(9-vinylcarbazole) (PVK) is a thermoplastic -conjugated polymer with high thermal and chemical stability. These characteristics are useful in electroluminescent devices and photorefractive materials [29]. The - * CTC studied here are based on the decreased -electron density of benzene rings containing nitro groups (electron acceptor) interacting with the -electron rich carbazolyl groups of PVK (electron donor). In this work we review some of our recent studies of absorption spectra of complexes between compounds of polyvinyl carbazole (PVK) were synthesized and trinitrofluorenone (TNF) were determined, (Figure 1).

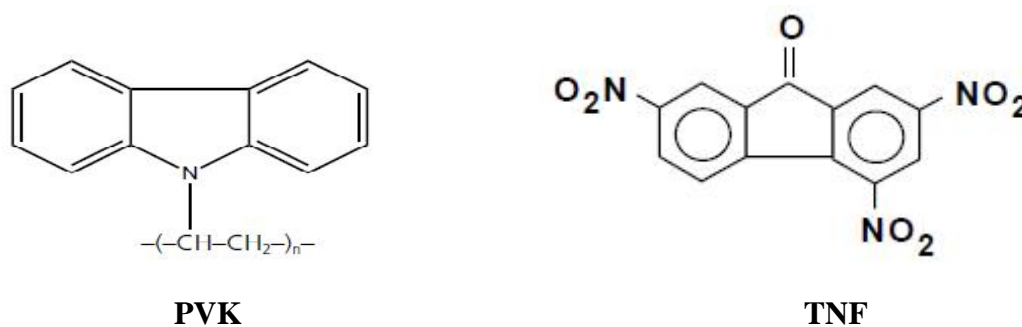


Fig.1. Chemical structure of PVK and TNF

Below-gap optical excitation of such organic donor/acceptor blends reveals subtle features attributed to CTC, which have recently attracted much attention by their property of extending optical absorption. One proposal is to use 2,4,7-trinitro-9-fluorenone (TNF). And TNF remains a model prototype for studying the influence of CTC states in organic photovoltaics. Recently a series of significant follow-up works on polymer/TNF blends has been performed [30,31].

2. EXPERIMENTAL

2.1. Apparatus

A spectrophotometer was used for UV-vis spectra using chloroform as the solvent, the infrared spectrum of the complexes was recorded using KBr discs on Shimadzu.

2.2. Materials

Commercially available monomer, N-vinyl carbazole (VCz, 98%), 2,4,7-trinitrofluorenone (TNF, 98%) which were purified by recrystallization, and benzoyl peroxide (98%).

The solvents toluene, methanol and petroleum ether were used either for synthesis or as precipitant agents.

2.2.1. Polyvinyl carbazole

Polyvinyl carbazole (PVK) was obtained by coupling 16 g of monomer, in this case vinyl carbazole (NVC), in 120 ml of (toluene). The catalyst in solution (benzoyl peroxide, in the same solvent) was added dropwise with vigorous stirring. 10^{-3} mol, relative to the monomer for 3 hours and at a fixed temperature at 60°C , was added dropwise with vigorous stirring, (figure 2). The resulting solution, after concentration in a Rotavapor, cooled and added drop by drop in 200 ml of MeOH during magnetic stirring, the precipitate obtained was filtered and washed with MeOH, and then dried in vacuo at a temperature of 40° .

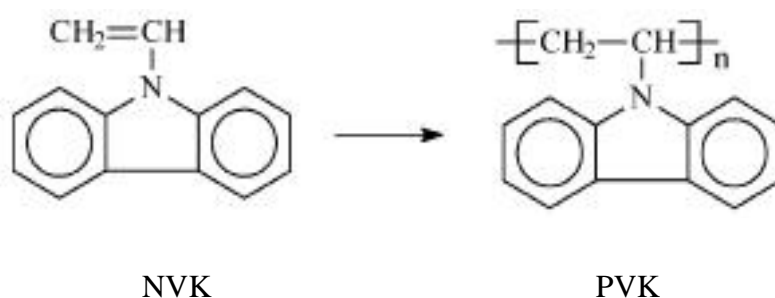


Fig.2. structure of monomer and polymer of vinyl carbazole

2.2.1.1. Infrared analysis

The FT-IR spectrum shows the majority of PVK peaks at $717,5\text{ cm}^{-1}$ assigned to the Ring deformation of substituted aromatic structure, at $744,5$ assigned to the CH_2 vibration and at $925, 1022, 1126, 1153, 1220, 1326, 1446, 1631, 2927$ and 3051 cm^{-1} corresponding to the C-C vibration, the C-C stretching, the C-H deformation in plane, the C-H deformation in plane of aromatic ring, C-N stretching, C-H deformation of vinylidene groups, the CH_2 stretching, C=C stretching of benzene respectively, C-H stretching and C-H of aromatic ring (figure 3).

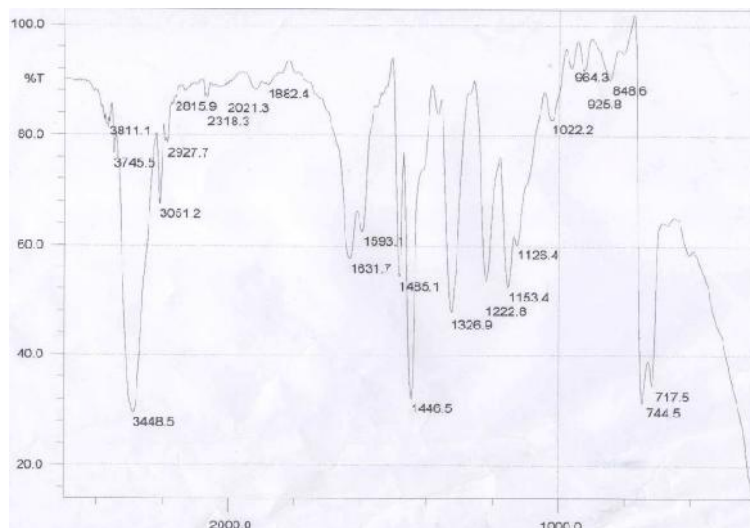


Fig.3. FT-IR spectra of PVK

2.2.2. Trinitrofluorenone (TNF)

2.2.2.1. Infrared analysis

The FT-IR spectrum (figure 4) shows the majority of TNF peaks at 1342,4 cm⁻¹, 1519,8 cm⁻¹, 1728,1 cm⁻¹, 1608 cm⁻¹, 3436,6 cm⁻¹ corresponding to the N = O, N-O, C=O, C=C, C-N, (Figure 4).

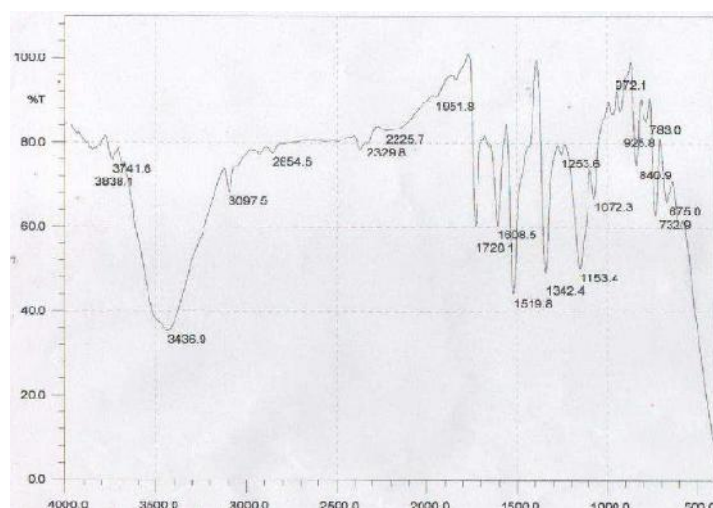


Fig.4. FT-IR spectra of TNF

2.3. Synthesis of CT complex

The solid CT complex of PVK and TNF was prepared by mixing equal weight of saturated solution of the donor in chloroform with saturated solution of acceptor. The actual percentage of CT complex 1/4, 1/2, 1/3, 1/1 in the mixture was stirred at room temperature and let to rest

overnight before analysis by UV-VIS spectroscopy.

3. RESULTS AND DISCUSSION

For the neat PVK one can see a band with maximum at about 332 nm and 347nm, the addition of the acceptor changed the absorption intensity to higher values. These measurements were based on the CT absorption bands exhibited by the spectra of the systems mentioned as above and was shown in (figure5).

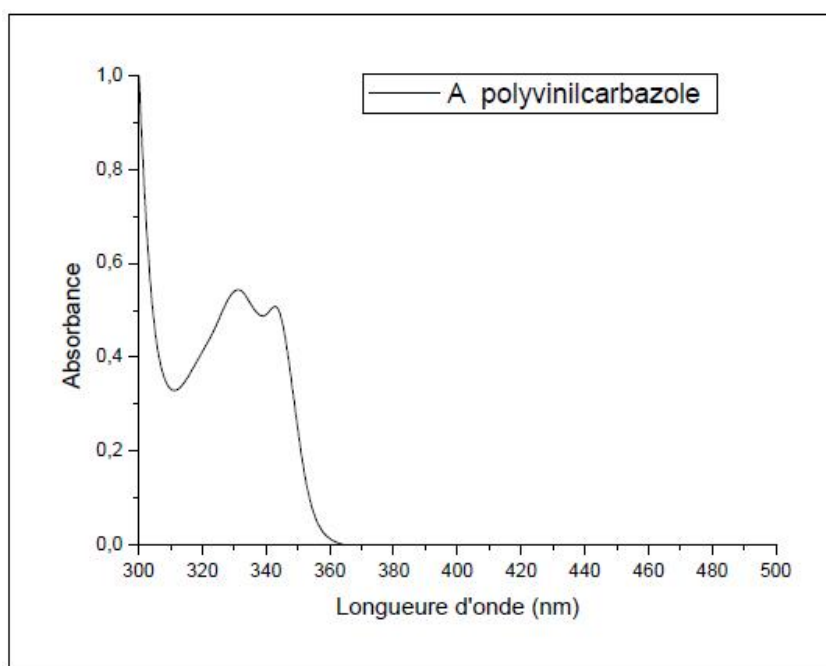


Fig.5. Absorption spectra of PVK

The new and low energy absorptions observed in solutions containing both donor and an acceptor have been described by Mullikan [32,33] as charge transfer transitions involving the excitation of an electron on the donor to an empty orbital on the acceptor.

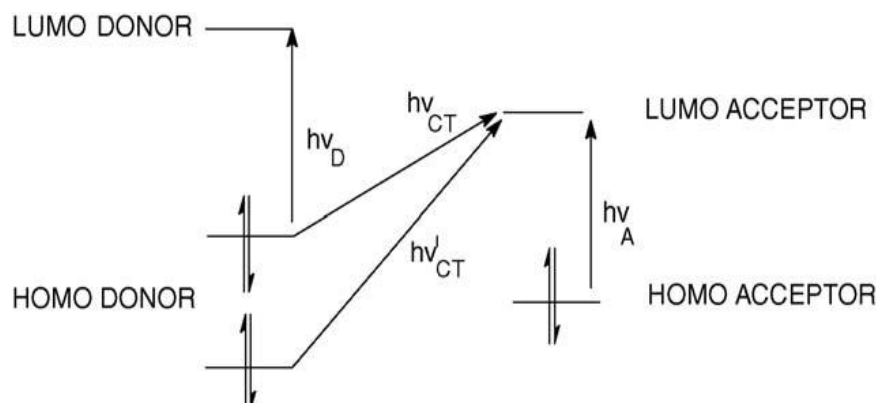


Fig.6. Charge transfer transitions for HOMO of the donor compounds and LUMO of the acceptor compounds

This is shown in (Figure 6) which $h\nu_{(CT)}$ depicts the energy of the CT transitions. The lowest energy CT transition will involve promotion of an electron residing in the highest occupied molecular orbital (HOMO) of the donor to the acceptor as shown for $h\nu_{(CT)}$. Charge transfer transitions involving electrons in lower energy orbitals also are possible and would result in higher energy CT transitions as shown $h\nu'_{CT}$. The complex showed two absorption maxima at around 250 and 400nm in solution, which correspond to the transitions of the complex's D/A ratio. Therefore, the D/A ratio is a very important parameter that can profoundly influence the device behavior. In general, it is necessary to optimize the D/A ratio to achieve the best performance. In the presented case, with varying weight ratios from 1: 1 (Figure 7).

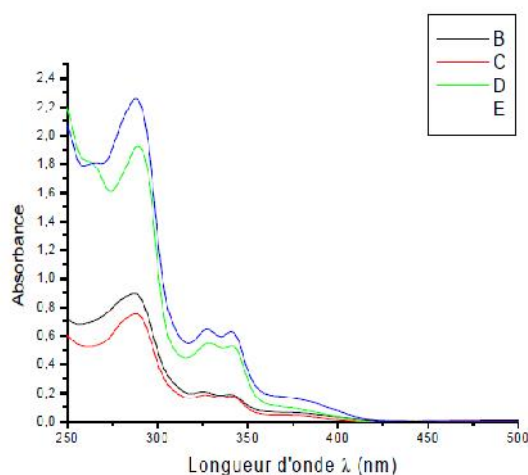


Fig.7. Absorption spectra of CT complex PVK/TNF

B: 1/4, C: 1/2, D: 3/4, E: 1/1

These spectra revealed the presence of the absorption bands that correspond to the CT interactions, PVK/TNF complex with ratio of 1/1 these compounds absorb maximally at 342nm, and it the biggest value than others deferent CT concentration.

4. CONCLUSION

Charge transfer complexation is important phenomenon in biochemical and bio electrochemical In this work, we have illustrated how the UV–Vis spectrophotometric method for the study of CTC of PVK with TNF reveals the formation of 1:1 (A:D) complex, and formation of CTC with PVK and TNF, From the conductivity of the CT Complex, it is obtained that the concentration of the donor is affected when it reacts with the acceptor and that when we increase the concentration of the donor.

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