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Original research article

Experimental and theoretical studies of the structural, electronic and optical properties of BCzVB organic material

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ABSTRACT

1,4-Bis[2-(3-*N*-ethylcarbazoryl)-vinyl]benzene (BCzVB) organic molecule in different solvents have been performed to explore its electronic structure and photophysical properties using solution technique and quantum chemistry calculations. The calculated energy levels of the BCzVB in solvent environments range from -5.04 to -5.06 eV (HOMO) and from -1.87 to -1.93 eV (LUMO). Solvent environment enhanced characteristic properties of the BCzVB. The performance of functional CAM-B3LYP and B3LYP was compared with measured the ultraviolet-visible (UV–vis) and charge transport properties. The refractive index was calculated using measured energy gap data. The atomic charges, dipole moments, total energies, lowest vibrational frequencies and radial distribution functions (RDFs) were searched. The reflectance spectra of the BCzVB solutions were also measured. From the results obtained, the BCzVB material has considerable potential for sensitivity, diode and OLED applications.

1. Introduction

Organic light-emitting diodes (OLEDs) have recently been drawn much attention in a wide range of applications [1–7], especially, in the panel displays and solid-state lightings [8,9].] To obtain high-performance OLEDs in the practical applications, it is always essential to achieve highly efficient OLEDs with simple structure [10–13]. According to this viewpoint, improving the device efficiency for OLEDs requires proper the energy levels [14], excellent luminescence efficiency [15], good balance of charge carrier properties [16], and excellent stability [17].

Among OLEDs, 1,4-Bis[2-(3-*N*-ethylcarbazoryl)-vinyl]benzene (BCzVB) gives an advantage to applications in material science because of its desirable properties for fabrication of new high-performance devices [18]. For example, a blue OLED based on the BCzVB organic molecule is used as a host in electro-phosphorescent devices in general [19–21]. Moreover, the efficiency and color purity of devices using the BCzVB organic material is remarkably improved [22]. Recently, the optoelectronic properties of the BCzVB were studied using solution technique [23]. Absorption and emission peaks were also determined for the BCzVB by solution method and EL spectra measurement, respectively [24]. In the literature, there is no any study on physical insight on the molecular mechanism of the BCzVB based on different solvent environments. Thus, the major point of this study is to explore the properties using a solution technique, and density functional theory (DFT) and time-dependent (TD)-DFT.

Firstly, we have checked whether the lowest vibrational frequency of the optimized geometry is on the potential energy surface with positive value or not. Then, some electronic properties were researched in different solvents. HOMO, LUMO, HUMO/LUMO gap

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and photoexcitation were calculated by B3LYP and CAM-B3LYP functionals and compared with the results obtained from the experiment. The refractive index based on the semi-empirical considerations, the radial distribution functions (RDFs) probability distribution, the curves based on photon energy and the reflectance spectrum were figured out.

2. Experimental details

We purchased the 1,4-Bis[2-(3-*N*-ethylcarbazoryl)-vinyl]benzene (BCzVB) and Dichloromethane (DCM), tetrahydrofuran (THF) and chloroform solvents from Sigma–Aldrich Co. We prepared three BCzVB materials for 0.72 *mM* using an Analytical Balance (AND-GR-200 Series). Then, these same materials were homogeneously dissolved in 13 mL volume of DCM, THF and chloroform solvents. Thus, the BCzVB solutions in the same molarity were prepared for different solvents. Finally, we recorded the UV spectra of the BCzVB with a UV-1800 Spectrophotometer (Shimadzu, Japan) at the range of 190–1100 nm.

3. Computational details

The most stable structures with positive vibration frequencies were obtained using DFT [25] with B3LYP/6–311 G (d, p) level [26–28]. To get reliable results, both B3LYP and CAM-B3LYP [29] functionals were used in the calculations because, especially for some molecular systems, excited state energy obtained from B3LYP functional gives better results [14] and underestimates excited-state energies in some cases [30–32]. Based on the optimized geometry obtained DFT/B3LYP/6–311 G(d,p), the absorbance spectra were performed using TD-DFT and compared with experimental values. The GAUSSIAN09 package was used in the calculations [33].

4. Results and discussion

4.1. Structural analysis

The optimized geometry with the lowest energy of BCzVB organic molecule is shown in Fig. 1. The lowest vibrational spectra are found as positive which means it is located at a stationary point on the potential energy surface. The lowest vibrational frequencies of the ground state were predicted as 8.5018, 7.8439 and 9.5106 for chloroform, DCM and THF solvents, respectively. The total energy of BCzVB in DCM (−1577.2529 a.u.) is also smaller than chloroform (−1577.2500 a.u.), THF (−1577.2522 a.u.) and gas phase (−1577.2385 a.u.). Lower energy and frequency correspond to more stable structure. Thus, it can conclude that the BCzVB compound in DCM is more stable than that of THF, chloroform and gas phase. The optimized structure is also found to be C_1 form.

4.2. UV spectra characteristics

We compared the UV spectra obtained from measurement with DFT and TD-DFT based on B3LYP and CAM-B3LYP functionals for the BCzVB materials of chloroform, THF and DCM solvents.Fig. 2(a–c) shows the experimental absorbance (Abs) and theoretical absorptivity for B3LYP and CAM-B3LYP models according to the wavelength (λ) of the BCzVB in chloroform, THF, and DCM solvents. As seen in Fig. 2(a–c), the BCzVB in different solvents and techniques displays small and large-scale peaks near ultraviolet (NUV) and visible (V) regions. From Fig. 2(a), the BCzVB in chloroform experimentally exhibits a maximum peak at 392 nm. The maximum peaks were found to be 451.26 and 383.39 nm B3LYP and CAM-B3LYP functionals, respectively. From Fig. 2(b), the BCzVB in THF shows maximum peaks at 392 nm by experiment and TD-DFT/CAM-B3LYP, respectively, but 451.13 nm for TD-DFT/ B3LYP. From Fig. 2(c), the BCzVB in DCM exhibits maximum peaks at 394, 387.72 and 451.98 nm for the experiment, CAM-B3LYP and B3LYP functionals, respectively. The results obtained indicate that the position (392 nm) of the maximum peak of the BCzVB for chloroform and THF solvents in experimental technique is the same, while the maximum peak, 394 nm, of the BCzVB in DCM solvent is different. This effect of the solvents is also observed for theoretical B3LYP. But, the positions of the maximum peaks of the BCzVB for theoretical CAM-B3LYP model are different from each other. From experimental results, we can conclude that TD-CAM-B3LYP gives better

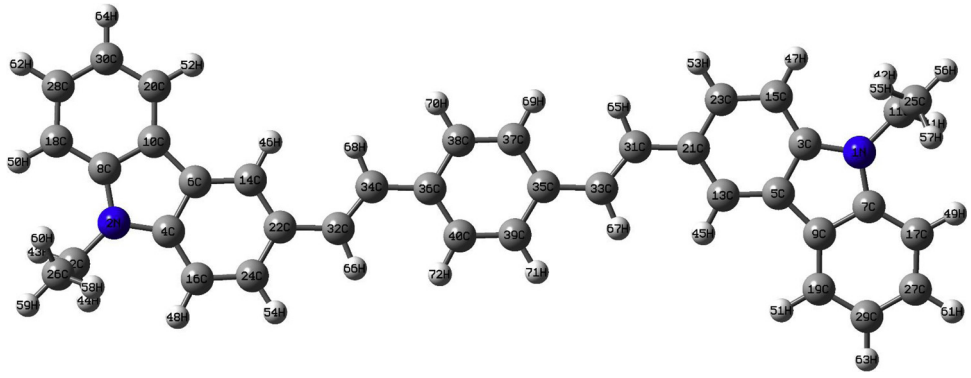

Fig. 1. Optimized ground state geometry of BCzVB with atom numbering calculated by B3LYP/6-311-G (d, p).

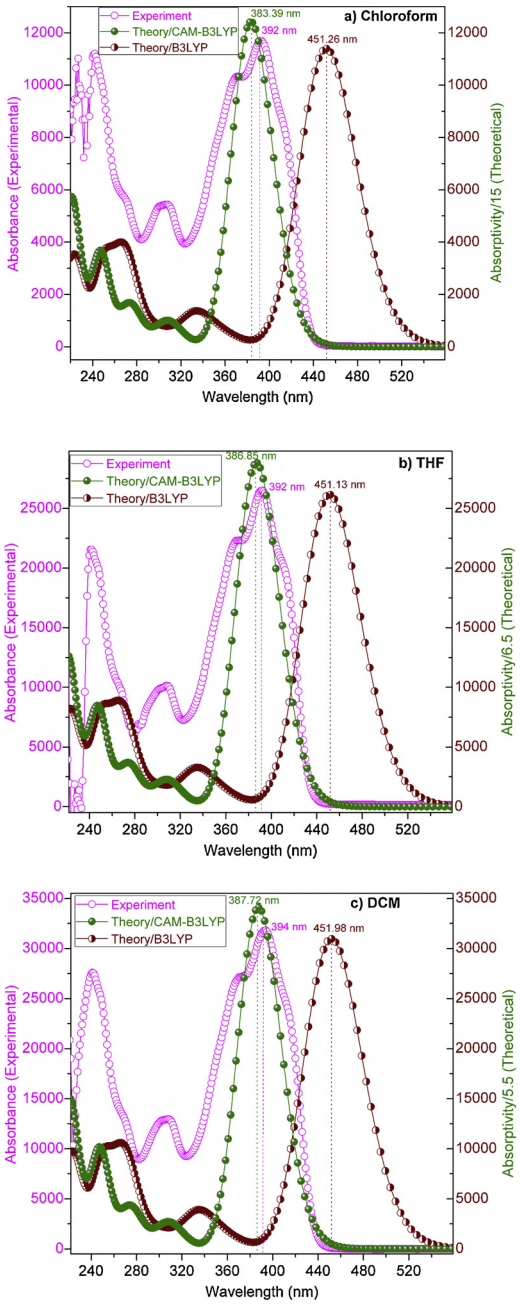

Fig. 2. The experimental and theoretical (for B3LYP and CAM-B3LYP functionals) molar absorptivity plots vs. wavelength (λ) of BCzVB organic material for a) chloroform b) THF and c) DCM solvents.

results than the theoretical TD-B3LYP, and the UV spectra of the BCzVB material can change with different solvents and techniques.

4.3. The band gap and refractive index relationship of BCzVB in different solvents

The band gap of the organic materials such as semiconductors is essential to determine their band structure, optical and optoelectronic properties. values can be estimated using the Tauc model [34]. Based on this model, the curves in terms of photon energy of the BCzVB in chloroform, THF and DCM were indicated in Fig. 3. The optical band gap values of BCzVB in chloroform, THF and DCM solvents from the experiment were found to be about 2.83, 2.82 and 2.80 eV, respectively. BCzVB exhibited the lowest for DCM solvent. Comparing electronic values obtained from (TD)-DFT with measured results (see Fig. 4), TD-DFT-B3LYP (3.13 eV) gives more reasonable result than that of CAM-B3LYP (5.37 eV).

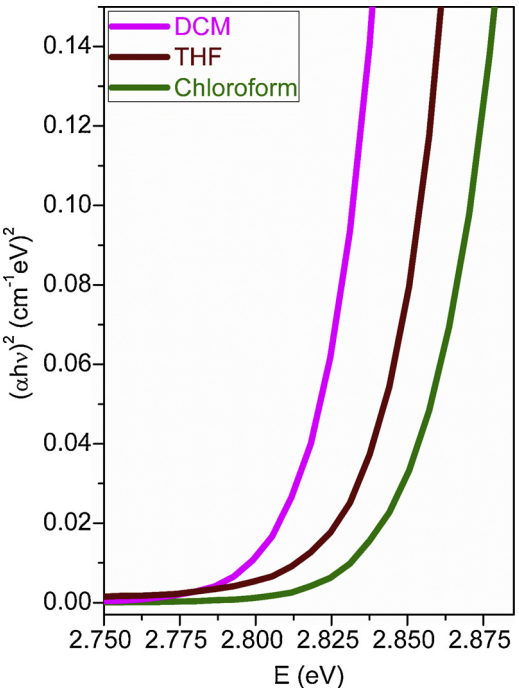

Fig. 3. The $(\alpha h\nu)^2$ vs photon energy (E) of BCzVB organic solutions for different solvents.

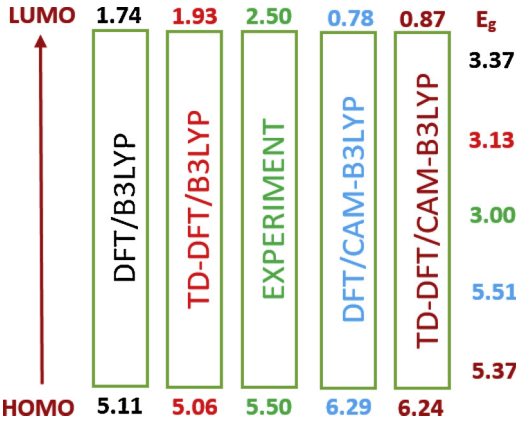

Fig. 4. Energy level diagram of BCzVB obtained from experiment and theory (for B3LYP and CAM-B3LYP functionals).

HOMO was found to be -5.11, -5.06, -5.50, -6.29 and -6.24 eV for DFT/B3LYP, TD-B3LYP, Experiment [35], CAM-B3LYP and TD/CAM-B3LYP, respectively. Similarly, LUMO was found to be -1.74, -1.93, -2.50, -0.78 and 0.87 eV for DFT/B3LYP, TD-B3LYP, Experiment [35], CAM-B3LYP and TD/CAM-B3LYP, respectively. The optical gap obtained from TD-DFT/ B3LYP (3.13 eV) was found to be compatible with the measured value (3.0 eV) [35].

The reflectance spectra are important to investigate the refractive index values of the materials. Fig. 5 shows spectra vs. λ of BCzVB for chloroform, THF and DCM. From Fig. 5, the reflectance of BCzVB varies with solvents and wavelengths and is almost constant after about 450 nm can be calculated depending on the reflectance or can be calculated depending on the optical.

The refractive index of the BCzVB organic molecule in chloroform, THF and DCM solvents for various relations [36] such as Kumar-Singh, Moss, Hervé-Vandamme, Ravindra and Reddy were searched. Also, we computed the average *n* values for these relations. Fig. 6 gives curves vs. solvents for the related relations. From Fig. 6, the BCzVB varies from about 2.35–2.83. The closest values of are observed for Kumar-Singh and Moss relations.

4.4. The atomic charges and dipole moments

The atomic charges computed in this study arise from the Mulliken population analysis. The charges of the BCzVB were tabulated in Table 1. Depending on the positions of the atoms in the structure, the charges of atoms display distinctive properties. For instance,

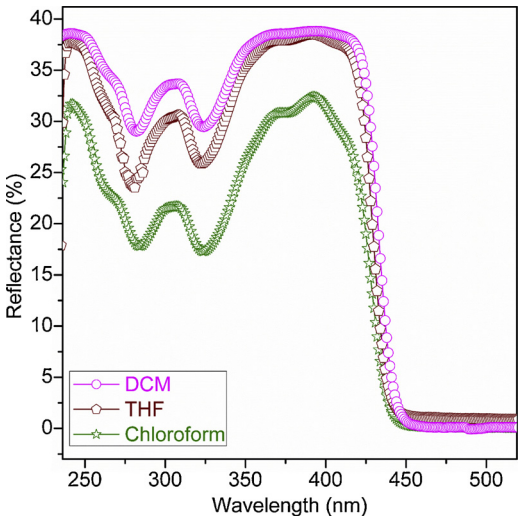

Fig. 5. The reflectance (R) vs. wavelength (λ) of BCzVB solutions for DCM, THF and chloroform solvents.

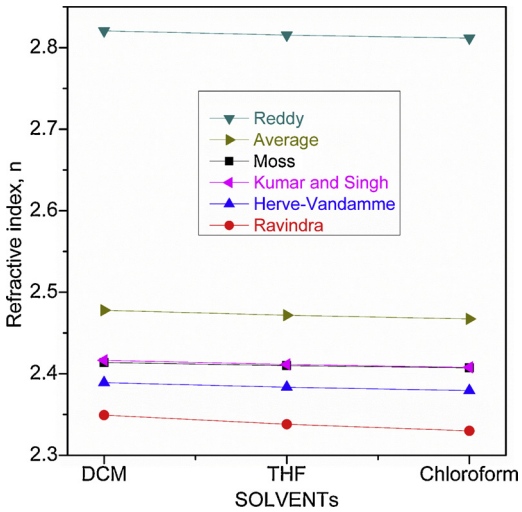

Fig. 6. The refractive index (n) curves solvents of BCzVB organic material for different relations.

carbon atoms (C3, C4) and (C5, C6) have positive and negative charges (see Fig. 1 for the positions of atoms and Table 1). Hydrogen atoms have positive charges since hydrogen is an acceptor atom.

The dipole moment results from differences in electronegativity. The bigger corresponds to stronger intermolecular interaction. The bigger value of the component of along the z-axis (= −2.3620 Debye) gives rise to large negative charge separation. The corresponding total was found as 2.3622 Debye. The value of the BCzVB molecule in DCM solvent is higher than that of chloroform (2.2790 Debye) and THF (2.3427 Debye) solvents. These values are compatible with the energy gap values because the lowest gap energy of BCzVB in DCM means easy excitation of electrons from HOMO to LUMO.

4.5. Radial Distribution Function (RDF)

The radial distribution functions (RDFs) was analyzed for C—C, C—N, C—H and H—H interactions in the BCzVB molecule (see Fig. 7). The RDFs of each atomic pairs was calculated using the optimized geometry of the BCzVB organic molecule. From Fig. 7, C—N has a narrower and higher distribution. C—C interaction is shorter than that of C—N and C—H for C atoms, while H—H interaction is shorter than that of the others. Considering all interaction pairs, C—N has a stronger interaction than that of the others. We also accomplish the probability distribution according to the coordination number to search the effect of interactions of the atoms in the BCzVB (see Fig. 8). The probability distribution of C—N interaction significantly decreases while it increases for H—H hydrogen bonding interaction based on the coordination number. Moreover, fluctuations in the probability distribution are seen for C—C and C—H interactions.

Table 1
Mulliken atomic charges of the BCzVB.

Atoms	Mulliken atomic charges	Atoms	Mulliken atomic charges
N1	−0.533912	C37	−0.055262
N2	−0.534293	C38	−0.082921
C3	0.251676	C39	−0.074480
C4	0.252985	C40	−0.063607
C5	−0.112930	H41	0.122883
C6	−0.114999	H42	0.122378
C7	0.236234	H43	0.122854
C8	0.236431	H44	0.122347
C9	−0.105354	H45	0.087359
C10	−0.106412	H46	0.087762
C11	−0.113202	H47	0.092353
C12	−0.113201	H48	0.092202
C13	0.009065	H49	0.093255
C14	0.015192	H50	0.093275
C15	−0.076202	H51	0.082327
C16	−0.077609	H52	0.082234
C17	−0.077621	H53	0.082800
C18	−0.077734	H54	0.083383
C19	−0.045282	H55	0.117189
C20	−0.045266	H56	0.106684
C21	−0.075825	H57	0.117176
C22	−0.078963	H58	0.117098
C23	−0.078043	H59	0.106667
C24	−0.073400	H60	0.117187
C25	−0.272763	H61	0.090353
C26	−0.272762	H62	0.090406
C27	−0.093906	H63	0.088881
C28	−0.093840	H64	0.088890
C29	−0.108201	H65	0.087573
C30	−0.108262	H66	0.088385
C31	−0.077512	H67	0.086629
C32	−0.082777	H68	0.086049
C33	−0.084346	H69	0.089555
C34	−0.078358	H70	0.080988
C35	−0.057613	H71	0.081745
C36	−0.052454	H72	0.088862

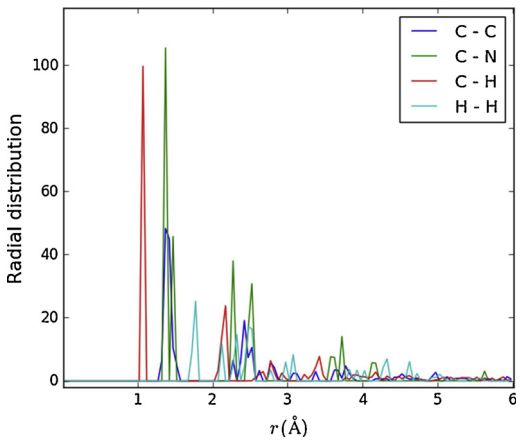

Fig. 7. Radial distribution functions (RDFs) of the carbon-carbon (C—C), carbon-nitrogen (C—N), carbon-hydrogen (C—H) and hydrogen-hydrogen (H—H) interactions for BCzVB.

5. Conclusions

The photophysical and optical features of the BCzVB organic molecule have been analyzed using solution technique and (TD)-DFT method. The results obtained show that the optimized structure is on the C_1 configuration. Comparing with experimental data, the B3LYP functional gives more reasonable the band energy than CAM-B3LYP functional, while CAM-B3LYP functional for the absorbance of photoexcitations is more precise than that of B3LYP functional. Depending on the total energy and lowest vibrational

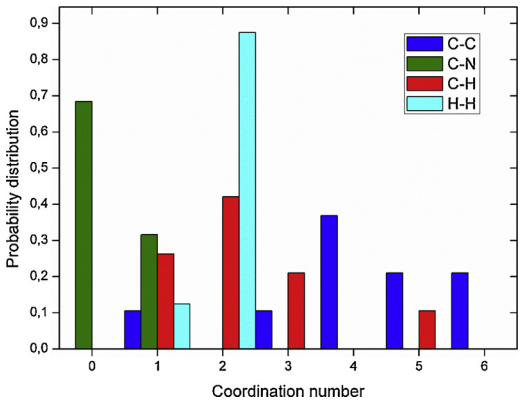

Fig. 8. Probability distributions of the carbon-carbon (C—C), carbon-nitrogen (C—N), carbon-hydrogen (C—H) and hydrogen-hydrogen (H—H) interactions for BCzVB.

frequency, the most stable structure of the BCzVB was obtained in DCM solvent. The RDFs and probability distribution of binary interactions were also computed. The refractive indices and band gaps in the different solvent environment were analyzed. The reflectance spectra in different were also investigated as a function of wavelength. The results obtained also show that DCM can be used for optical devices because the BCzVB in DCM gives desirable results such as low optical band gap, high mass extinction coefficient, and reflectance as well as has proper parameters for sensitivity, diode, and OLED applications.

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