

Tuning optoelectronic properties of carbazole through substituent effect: TD-DFT investigation

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Abstract

π -conjugated organic materials such as carbazoles have attracted much attention because of their applications in electronic devices such as OLED's, solar cells and sensors. Due to their optoelectronic properties, high charge carrier mobility, suitable band gaps and orbital energies, carbazoles have received immense attention to serve as a potent photosensitizer for obtaining high performance in DSSC. The present QSPR study of substituted carbazole and carbazole anion with electron donor (NH_2) and acceptor (NO_2) substituents at various positions is done by the density functional theory (DFT) calculations at B3LYP/6-31G(d,p) level. The longest maximum absorption wavelengths (λ_{max}) in vacuum as well as in polar (acetonitrile) and non-polar (benzene) solvents are studied by using the time-dependent density functional theory (TD-DFT). For the singly substitution of NH_2 (at C3) and NO_2 (at C4) groups to the carbazole and its anion, the λ_{max} values are observed to be shifted to the longest wavelength from 290.56 nm to 325.73 and 375.77 nm than the other respective positions. Whereas, the respective λ_{max} values for carbazole-anion are found at 384.28 and 590.53 nm respectively. For disubstituted carbazole with NH_2 and NO_2 at C3 and C4 positions, the longest λ_{max} shifts to 477.15 nm and for carbazole-anion the longest λ_{max} obtained at C4 (NH_2) and C5 (NO_2) positions with λ_{max} value 694.61 nm. Similar observations are also found in acetonitrile and benzene solvents. Further, it is observed that as the λ_{max} increases, the HOMO-LUMO energy gap (E_{HL}) value decreases accordingly which can be attributed to intramolecular charge transfer from NH_2 to NO_2 groups. A very good correlation of λ_{max} with E_{HL} is observed with correlation coefficient between 0.91 to 0.95 in vacuum as well as in acetonitrile and benzene solvents. Present study may provide valuable guidelines for the choice of suitable substituent to design carbazole moieties as efficient photosensitizer in DSSC. Copyright © 2017 VBRI Press.

Keywords: Topology, carbazole, π -conjugation, UV/Vis spectrum, TD-DFT.

Introduction

From the last few years, organic π -conjugated optoelectronic functional materials have attracted increasing attention due to their applications in electronic devices such as OLEDs [1], solar cell [2], non-linear optical device [3] and sensors [4]. It is easy to tune optoelectronic properties of organic functional material by incorporating the hetero atom into their π -conjugated system. Carbazole is an organic heterocyclic compound consisting of a dibenzopyrrole structure [5]. Carbazole and substituted carbazole are known for their unique photophysical properties and intense luminescence [6]. Naturally occurring carbazole was first isolated from murrayanine from *Murraya koenigii* Spreng. In India, the leaves of this small tree are known as currypatta [7]. The substituent attached to π -conjugated polymers containing carbazole units at

various positions have received increasing attention because of their unique electronic properties, their high photoluminescence quantum efficiency and thermal stability [8-11]. The substituted carbazole with donor- π -acceptor (D- π -A) nature possesses properties such as high charge carrier mobility, suitable band gaps and orbital energies that are important for obtaining more efficiency in solar cells [2, 12-13]. Due to unique optical and electronic properties and potential low cost, these organic materials have been used quite extensively in the electronic devices. Especially, because of the existence of the many modification sites makes it an attractive photosensitizer in dye sensitized solar cells (DSSC) [14-22]. After the successful synthesis of N-alkyl-2, 7- diiodocarbazole 2, 7-disubstituted carbazole became the promising candidate with more planar and well delocalized π -electron structure for

the applications of organic photovoltaic materials [23]. Alimi *et al.* [24] have investigated the photo-physical properties of carbazole oligo-thiophene-phenylene derivatives. They suggested that these derivatives act as good hole/electron transporting materials. The topological connectivity of the substituents to the carbazole moiety affects its polymer properties. The conjugated copolymers of electron donating (2, 7-carbazolylene) and electron accepting π -conjugated systems were found to be very suitable as p-type semiconductor for bulk heterojunction solar cells [25-28]. These findings stimulated renewed interests in the development of conjugated carbazole polymers with different connectivities. Ejsmont *et al.* [29] have studied the effect of NO₂ substituent on electronic structure of aromatic systems by harmonic oscillator model of aromaticity (HOMA) which is the descriptor of π -electron delocalization. They found that the HOMA value decreases when NO₂ is substituted at aromatic ring as compared to NO₂ substituted at five membered hetero cyclic pyrrole. The topology of conjugated system with donor and acceptor [30] groups has been widely studied for their applications in transparent conductors [31-33], LEDs [34-36], thin film transistors [37-38] and photovoltaic devices. The quantitative structure-property relationship (QSPR) study of lawsone molecule by Ware and Pingale [39] have reported the analysis of lawsone derivatives substituted with various electron-donating and withdrawing groups for the application of dye sensitized solar cell (DSSC) to enhance maximum absorption at longer wavelength in the visible region by using time-dependent density functional theory (TD-DFT) approach. This study suggested that the dye molecule with a donor-acceptor substituent system at positions can extend maximum absorption at longer wavelength in visible region of solar spectrum. Sun *et al.* [40] have synthesized new dyes containing carbazole with various donor (carbazole, iminodibenzyl, and phenothiazine) and acceptor (cyanoacrylic acid and acrylic acid) substituents. Their DFT based study shown that due to the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) excitation, electron density moves from donor to acceptor substituents. The electronic transition of absorption spectrum derived by TD-DFT method has provided useful structural and electronic information for designing novel conducting organic polymer materials [41].

In the present work, we elucidate the theoretical view of UV-Visible (UV/Vis) spectral features of unsubstituted and substituted carbazole and carbazole-anion and also their QSPR analysis to design a more efficient photosensitizer for DSSC with enhanced maximum absorption at longer wavelength (λ_{\max}) in the visible region by substituting donor and acceptor groups at various positions. The various positions of substitutions of carbazole and its

anion are shown in **Fig. 1**. The acceptor and donor groups include NO₂ and NH₂ respectively as test cases. The HOMO-LUMO energy gap (E_{HL}) which is one of the most important photo-physical properties, is used to explore the relationship with respective λ_{\max} of carbazole moieties.

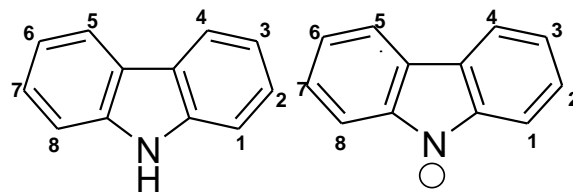


Fig. 1. Carbazole and Carbazole-anion molecules with numbered positions for substitutions.

Methodology

The geometries of carbazole (Cbz) and carbazole anion (Cbz-anion) having substitution of electron donating (NH₂) and withdrawing (NO₂) groups are optimized at B3LYP/6-31G(d,p) level of theory. (cf. **Figs. 1** and **2** for the respective structures) The optimized geometries are taken for the frequency calculation and verified that the obtained structures are minima on the potential energy surface with zero imaginary frequencies. The optimized geometry of each structure is further used to determine longest λ_{\max} using the TD-DFT/ PBE1PBE/ 6-31G(d,p) method [42-44]. All the calculations are performed with the Gaussian09 program [45]. Among the several approaches proposed to describe the solvent effect, the conductor like polarizable continuum model (C-PCM) [46-47] is quite popular, due to its flexibility, efficiency and for the accurate prediction of transition wavelengths of the molecules. Here, the C-PCM model is employed to consider the implicit effect of solvent. The optimized structures and frontier molecular orbitals are visualized with UNIVIS software [48].

Results and discussion

To gain insights into the effect of donor and acceptor substituents on Cbz and Cbz-anion at various positions, the different structures shown in **Fig. 2** are optimized. The λ_{\max} and E_{HL} values for each Cbz moieties are calculated. The λ_{\max} of unsubstituted Cbz (cf. **Fig. 2i**) in vacuum is observed at 290.56 nm with oscillator strength (f) and E_{HL} values of 0.0312 and 5.165 eV respectively. A singlet excited state with a non-zero f value provides information of an allowed transition (see **Table 1**). In polar acetonitrile solvent, the λ_{\max} is observed as 293.92 nm with E_{HL} value of 5.128 eV. This λ_{\max} value in acetonitrile is in good agreement with the experimental one obtained by Boo *et al.* [49] i.e. 289 nm. In non-polar benzene solvent, the calculated λ_{\max} is observed as 293.27 nm with E_{HL} value 5.146 eV.

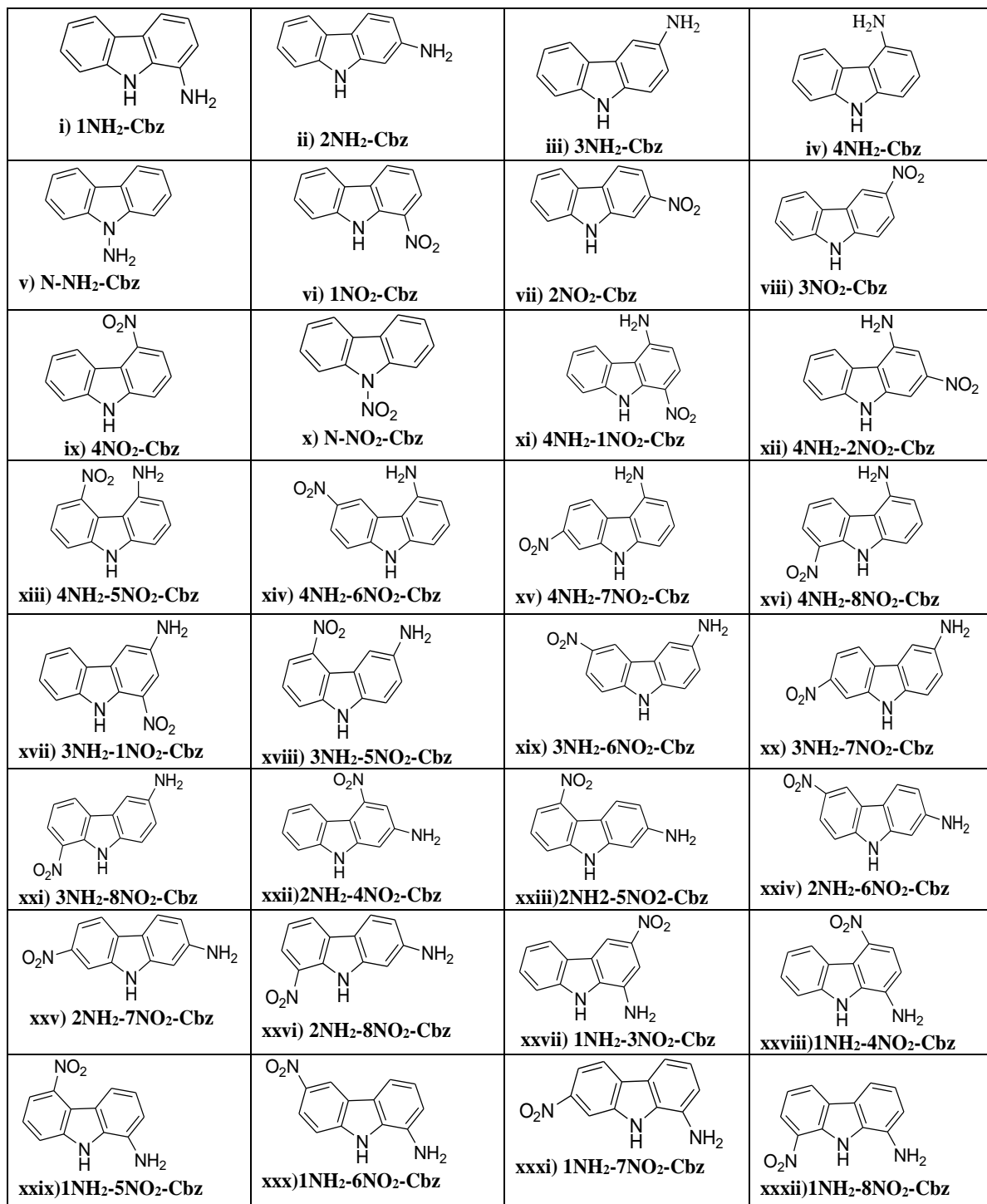


Fig. 2 Schematic structures of substituted carbazole with different topological connectivity of donor (NH₂) and withdrawal (NO₂) groups.

As shown in **Table 1**, the λ_{\max} of Cbz in polar and non-polar solvents are qualitatively similar in nature and are quite closer to the visible region in vacuum. These values of Cbz are considered as the reference for substituted Cbz with NH₂ and NO₂ groups. When only an NH₂ group is attached to the Cbz at positions C1, C2, C3, C4 separately (see **Fig.2**.ii, iii, iv and v respectively) and N (*cf.* **Table S1**). It is observed that λ_{\max} shifts to longest wavelength at position C3 (3NH₂) in vacuum at value 325.7 nm and the E_{HL}

value for the same observed at 4.578 eV. In both the solvents acetonitrile and benzene the longest λ_{\max} values are found at 331.9 and 330.7 nm and E_{HL} values at 4.530 and 4.553 eV respectively.

With the singly substituted donating NH₂ group to the Cbz the λ_{\max} enhances maximum at position C3 (3NH₂) by 26.71 nm in vacuum. Similar, enhancement in λ_{\max} is observed in both the solvents. In case of attachment of single NO₂ the λ_{\max} value is observed as highest when attached at the position C4

(4NO₂) i.e. 375.7, 405.6 and 391.6 nm in vacuum, acetonitrile and benzene when compared to the other remaining NO₂ substitutions. Out of all the singly substituted positions only one shifted λ_{\max} value is reached in visible region i.e. 405.6 nm when NO₂ group is attached to position C4 (4NO₂) in acetonitrile solvent. With the singly substitution at 3NH₂ and 4NO₂ groups to Cbz in vacuum, λ_{\max} shift from 290.36 to 325.73 and 375.77 nm respectively. In case of unsubstituted Cbz-anion, (cf. **Table 1**) the λ_{\max} in vacuum is observed at 361.98 nm and E_{HL} value of 3.092 eV.

In polar acetonitrile solvent, the λ_{\max} is observed as 349.53 nm and E_{HL} value 4.450 eV. In non-polar benzene solvent, the λ_{\max} is observed at 356.98 nm

For Cbz-anion similar sites like Cbz are observed for longest shift of λ_{\max} at 3NH₂ and 4NO₂ singly substitution separately and shift the values from 361.98 to 384.18 and 590.53 nm respectively. As compared to Cbz, the Cbz-anion shows longer absorption wavelength in visible region, when only withdrawing substituent is attached to position C4. (cf. **Table 1**) **Table 2** and **Table S1** brings out that in doubly substituted Cbz moieties, the NH₂ at C3 and NO₂ at C5 shows longest shift of λ_{\max} at 477.15 in vacuum and 522.23 and 501.07 nm in acetonitrile and benzene respectively. However, for the Cbz-anion substitution, longest λ_{\max} are observed for NH₂ at C4 and NO₂ at C5 position with values 694.61, 671.95 and 687.59 nm in vacuum, acetonitrile and benzene

Table 1. Longest maximum absorption wavelength (λ_{\max}), Oscillator Strength (f) and HOMO-LUMO energy gap (E_{HL}) of donating (NH₂) and withdrawing (NO₂) substituents at various positions of Carbazole (Cbz) in Vacuum, Acetonitrile and Benzene solvents for singly substituted carbazole calculated at TD-DFT/PBEPBE/6-31G(d,p) level. As of symmetry substitution to only one benzene ring is carried out. The values in bracket are for the respective substituted structure for carbazole-anion (Cbz-anion). (See **Fig. 2** for details).

System	Vacuum			Acetonitrile			Benzene		
	λ (nm)	f	E _{HL} (eV)	λ (nm)	f	E _{HL} (eV)	λ (nm)	f	E _{HL} (eV)
Cbz	290.56 (361.98)	0.0312 (0.0230)	5.165 (3.092)	293.92 (349.53)	0.0470 (0.0371)	5.128 (4.450)	293.27 (356.98)	0.0515 (0.0384)	5.146 (4.387)
1NH₂-Cbz	297.02 (357.56)	0.0514 (0.0376)	4.990 (4.311)	302.00 (349.68)	0.0774 (0.0591)	4.927 (4.394)	300.75 (355.08)	0.0846 (0.0618)	4.959 (4.355)
2NH₂-Cbz	284.97 (352.84)	0.0954 (0.0175)	4.980 (4.422)	289.79 (339.43)	0.4168 (0.0271)	4.940 (4.567)	289.79 (347.05)	0.4580 (0.0291)	4.962 (4.496)
3NH₂-Cbz	325.73 (384.18)	0.0495 (0.0249)	4.578 (4.077)	331.95 (374.58)	0.0702 (0.0408)	4.530 (4.159)	330.75 (380.80)	0.0785 (0.0420)	4.553 (4.122)
4NH₂-Cbz	299.03 (357.51)	0.0946 (0.0279)	4.956 (4.355)	303.02 (344.85)	0.1399 (0.0436)	4.927 (2.893)	302.79 (352.32)	0.1563 (0.0455)	4.941 (4.426)
1NO₂-Cbz	368.84 (452.49)	0.1183 (0.1238)	4.087 (3.415)	389.61 (462.25)	0.1652 (0.1888)	3.919 (3.351)	382.52 (463.40)	0.1757 (0.1913)	4.001 (3.387)
2NO₂-Cbz	360.45 (551.86)	0.0267 (0.0250)	4.183 (2.952)	397.37 (549.77)	0.0319 (0.0331)	3.861 (2.977)	379.53 (553.56)	0.0387 (0.0380)	4.019 (2.966)
3NO₂-Cbz	319.48 (413.75)	0.0749 (0.1807)	4.556 (3.460)	352.33 (427.40)	0.1432 (0.2509)	4.175 (3.418)	336.93 (427.03)	0.1631 (0.2910)	4.363 (3.438)
4NO₂-Cbz	375.77 (590.53)	0.0342 (0.0235)	4.074 (2.855)	405.64 (569.77)	0.0448 (0.0364)	3.833 (2.933)	391.62 (584.30)	0.0507 (0.0373)	3.955 (2.893)

and E_{HL} value 4.387 eV. All the values of λ_{\max} are shifted towards the longer wavelength by 71.42, 55.61 and 63.71 nm and the E_{HL} values reduces by 2.073, 0.678 and 0.759 eV in vacuum, acetonitrile and benzene solvent respectively as compared to unsubstituted Cbz. These λ_{\max} values of unsubstituted Cbz-anions are considered as the reference for substituted Cbz-anion with NH₂ and NO₂ groups. When only NH₂ is attached to the Cbz-anion at positions C1, C2, C3 and C4 separately (see **Fig. 1**), it is observed that λ_{\max} shifted to longer wavelength at position C3 in vacuum 384.18 nm and in both the solvents, acetonitrile 374.58 nm and in benzene 380.80 nm respectively as compared with the respective unsubstituted Cbz-anion i.e. 361.98 nm in vacuum, 349.53 nm in acetonitrile and 356.98 nm in benzene. In case of only NO₂ the λ_{\max} values are highest at the position C4 i.e. 590.53, 569.77 and 584.30 nm in vacuum, acetonitrile and benzene respectively as compared to all the other positions.

respectively. This brings out that the Cbz-anion substituted moieties are having longer λ_{\max} values than Cbz ones. Furthermore, it is seen that in doubly substituted Cbz the λ_{\max} is observed to be in longer visible region in polar acetonitrile solvent as compared to vacuum and nonpolar benzene solvent. While in case of Cbz-anion maximum absorption is observed in vacuum and non-polar benzene solvent at all positions as compared to polar acetonitrile solvent. With the substitution of donor and acceptor groups at proper position one can tune the λ_{\max} in longer visible region for efficiency enhancement in Cbz photosensitizer based DSSCs. Substituting the donating and withdrawing substituents simultaneously at different positions of Cbz, generally it is observed that λ_{\max} shift to longer wavelength than the singly substituted ones. In doubly substituted Cbz the maximum absorption wavelength is observed to be in longer visible region in polar acetonitrile solvent as compared to vacuum

Table 2. Longest maximum absorption wavelength (λ_{\max}), Oscillator strength (f) and energy difference between HOMO and LUMO (E_{HL}) of NH_2 and NO_2 substituted carbazole. Italics values in brackets are for respective substitutions to carbazole-anion. (See Fig. 2 for details).

System	Vacuum			Acetonitrile			Benzene		
	λ (nm)	(f)	E_{HL} (eV)	λ (nm)	(f)	E_{HL} (eV)	λ (nm)	(f)	E_{HL} (eV)
4NH₂-1NO₂-Cbz	341.34 (421.41)	0.1623 (0.1327)	4.172 (3.610)	360.01 (427.80)	0.2515 (0.2035)	3.973 (3.548)	354.93 (429.77)	0.2727 (0.2082)	4.073 (3.173)
4NH₂-2NO₂-Cbz	391.65 (555.87)	0.0831 (0.0369)	3.876 (2.916)	438.57 (562.60)	0.0948 (0.0530)	3.564 (2.912)	417.55 (562.92)	0.1151 (0.0587)	3.716 (2.916)
4NH₂-5NO₂-Cbz	475.49 (694.61)	0.0513 (0.0181)	3.334 (2.552)	514.87 (671.95)	0.0584 (0.0279)	3.160 (2.616)	497.55 (687.59)	0.0708 (0.0292)	3.247 (2.582)
4NH₂-6NO₂-Cbz	366.55 (417.81)	0.0991 (0.2395)	3.983 (3.361)	408.70 (438.29)	0.1418 (0.3463)	3.620 (3.263)	389.39 (435.73)	0.1534 (0.3793)	3.797 (3.313)
4NH₂-7NO₂-Cbz	392.82 (557.95)	0.0669 (0.0164)	3.775 (2.914)	442.30 (568.64)	0.0737 (0.0194)	3.423 (2.876)	418.60 (565.26)	0.0928 (0.0233)	3.597 (2.898)
4NH₂-8NO₂-Cbz	417.18 (453.17)	0.1145 (0.1593)	3.608 (3.364)	452.52 (474.94)	0.1397 (0.2348)	3.385 (3.222)	438.05 (469.99)	0.1588 (0.2409)	3.495 (3.302)
3NH₂-1NO₂-Cbz	434.16 (489.34)	0.1221 (0.1387)	3.505 (3.113)	471.84 (507.99)	0.1500 (0.2143)	3.302 (3.009)	458.59 (506.80)	0.1665 (0.2159)	3.401 (3.068)
3NH₂-5NO₂-Cbz	477.15 (659.38)	0.0216 (0.0224)	3.328 (2.619)	522.33 (655.71)	0.0291 (0.0334)	3.108 (2.628)	501.07 (663.14)	0.0317 (0.0347)	3.217 (2.623)
3NH₂-6NO₂-Cbz	381.45 (446.91)	0.0671 (0.1338)	3.859 (3.273)	436.65 (479.86)	1.0000 (0.1723)	3.430 (3.121)	409.45 (468.24)	0.1082 (0.2054)	3.642 (3.200)
3NH₂-7NO₂-Cbz	428.41 (587.21)	0.0492 (0.0415)	3.513 (2.763)	488.72 (610.07)	0.0629 (0.0632)	3.149 (2.682)	459.14 (601.62)	0.0717 (0.0673)	3.330 (2.729)
3NH₂-8NO₂-Cbz	450.05 (490.60)	0.0546 (0.0967)	3.412 (3.204)	490.35 (519.99)	0.0760 (0.1314)	3.176 (3.039)	472.31 (509.63)	0.0807 (0.1420)	3.293 (3.125)
2NH₂-4NO₂-Cbz	402.86 (611.15)	0.1066 (0.0231)	3.777 (2.774)	446.72 (584.85)	0.1170 (0.0377)	3.506 (2.853)	427.21 (602.62)	0.1423 (0.0378)	3.645 (2.813)
2NH₂-5NO₂-Cbz	396.68 (576.76)	0.1792 (0.0207)	3.728 (2.909)	441.82 (567.84)	0.2079 (0.0318)	3.431 (2.942)	422.50 (575.46)	0.2436 (0.0328)	3.584 (2.926)
2NH₂-6NO₂-Cbz	364.38 (411.07)	0.0156 (0.1257)	4.053 (3.479)	416.36 (431.81)	0.0232 (0.0740)	3.607 (3.408)	389.45 (424.92)	0.0257 (0.2059)	3.829 (3.444)
2NH₂-7NO₂-Cbz	359.68 (543.84)	0.4581 (0.0149)	3.865 (2.998)	406.19 (546.46)	0.5244 (0.0160)	3.483 (2.999)	388.15 (547.15)	0.5987 (0.0209)	3.676 (3.001)
2NH₂-8NO₂-Cbz	415.10 (442.09)	0.0672 (0.1346)	3.613 (3.460)	458.75 (456.20)	0.0782 (0.2172)	3.341 (3.354)	438.40 (455.05)	0.0949 (0.2157)	3.476 (3.324)
1NH₂-3NO₂-Cbz	344.61 (433.58)	0.1031 (0.2009)	4.277 (3.290)	387.67 (457.93)	0.1423 (0.2621)	3.881 (3.199)	367.79 (454.04)	0.1619 (0.3001)	4.076 (3.243)
1NH₂-4NO₂-Cbz	357.70 (522.61)	0.0949 (0.0487)	4.115 (3.022)	386.31 (514.27)	0.1449 (0.0823)	3.838 (3.046)	374.38 (523.36)	0.1544 (0.0822)	3.981 (3.035)
1NH₂-5NO₂-Cbz	416.32 (641.96)	0.0247 (0.0211)	3.718 (2.672)	477.27 (638.27)	0.0274 (0.0305)	3.333 (2.681)	444.77 (644.46)	0.0346 (0.0323)	3.536 (2.676)
1NH₂-6NO₂-Cbz	349.71 (444.34)	0.1175 (0.1798)	4.146 (3.254)	412.42 (470.82)	0.1608 (0.2469)	3.579 (3.133)	380.34 (464.32)	0.1807 (0.2754)	3.869 (3.194)
1NH₂-7NO₂-Cbz	391.99 (579.91)	0.0228 (0.0322)	3.821 (2.790)	463.23 (599.36)	0.0219 (0.0388)	3.319 (2.731)	425.25 (592.83)	0.0300 (0.0463)	3.576 (2.762)
1NH₂-8NO₂-Cbz	427.37 (491.01)	0.0844 (0.1087)	3.574 (3.180)	475.63 (513.97)	0.1073 (0.1557)	3.275 (3.057)	453.53 (508.72)	0.1205 (0.1624)	3.426 (3.121)

and nonpolar benzene solvent. This highlights that the effect of solvent also plays an important role in deciding λ_{\max} at the positions of substituents.

The E_{HL} values for Cbz and Cbz-anion are 5.165 and 3.092 eV respectively. For the longest λ_{\max} structure 3NH₂-5NO₂ from the all doubly substituted ones of Cbz the E_{HL} value observed at 3.328 eV. However, for the longest λ_{\max} structure of doubly substitution Cbz-anion 4NH₂-5NO₂, the E_{HL} value lowers to 2.552 eV. All the transitions show highest f value as reported in Table 1 and 2 for HOMO to LUMO transitions. It is important to examine the lowering of the E_{HL} of the doubly substituted Cbz and

Cbz-anion with donor and withdrawal groups at different positions. Fig. 3 shows the frontier molecular orbitals HOMO and LUMO of Cbz, Cbz-anion of the lowest E_{HL} valued structures of disubstituted Cbz and Cbz-anion. In disubstituted Cbz, the intramolecular charge transfer is observed when NH₂ group is at position C3 and NO₂ at position C5. The corresponding HOMO [Fig. 3(v)] of this structure shows more electron localization at donating group NH₂ which is shifted to NO₂ in its LUMO [Fig. 3(vi)]. Here intramolecular hydrogen bonding is observed between NH₂ and NO₂ group which may enhance the charge transfer.

Intramolecular charge transfer is observed also for lowest E_{HL} valued structure 4NH₂-5NO₂ of cbz-anion. The intramolecular charge transfer is also observed from its HOMO [Fig. 3(vii)] to LUMO [Fig.3(viii)] In view of the increase in λ_{max} and decrease in E_{HL} for other than N substitutions, the correlation between E_{HL} and λ_{max} of the doubly substituted Cbz is investigated and the correlation coefficient (R^2) is observed to be 0.94, 0.91 and 0.94 in vacuum [Fig.4(i)], polar acetonitrile [Fig.4(iii)] and non polar benzene [Fig.4(vi)] solvent. Here E_{HL} plays an important role for the longer shift of λ_{max} with smaller value of E_{HL} . Likewise, the good correlation between E_{HL} and λ_{max} of disubstituted Cbz-anion is observed with R^2 as 0.94, 0.93 and 0.95 in vacuum [Fig. 4(ii)], polar acetonitrile [Fig. 4(iv)] and non-polar benzene [Fig. 4(vi)] solvents

respectively. It is observed that as the λ_{max} increases, the E_{HL} decreases. This good correlation brings out that in Cbz-anion as well as Cbz for the higher λ_{max} and lower E_{HL} , major contribution comes from HOMO to LUMO transitions.

Conclusion

The UV/Vis spectral features of Cbz and substituted Cbz and their anionic forms are investigated with DFT and TD-DFT calculations. To gain a better understanding of the role of topology of electron donating and withdrawing substituents on Cbz and its anion, the QSPR study based on λ_{max} is carried out to design a better photosensitizer for DSSC. In Cbz and Cbz-anion, λ_{max} is studied at various possible positions of electron donating and withdrawing group. Substituting the NH₂ and NO₂ groups at C3

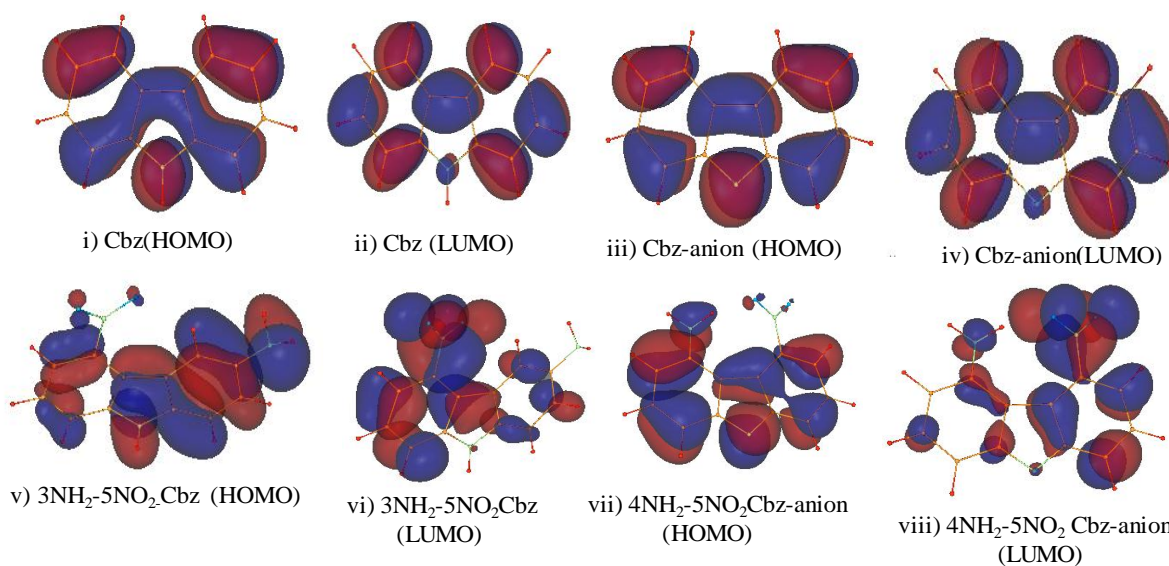


Fig. 3. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) isosurface value 0.0245 a.u. for carbazole and doubly substituted carbazole corresponding to longest λ_{max} in vacuum. (See text for details)

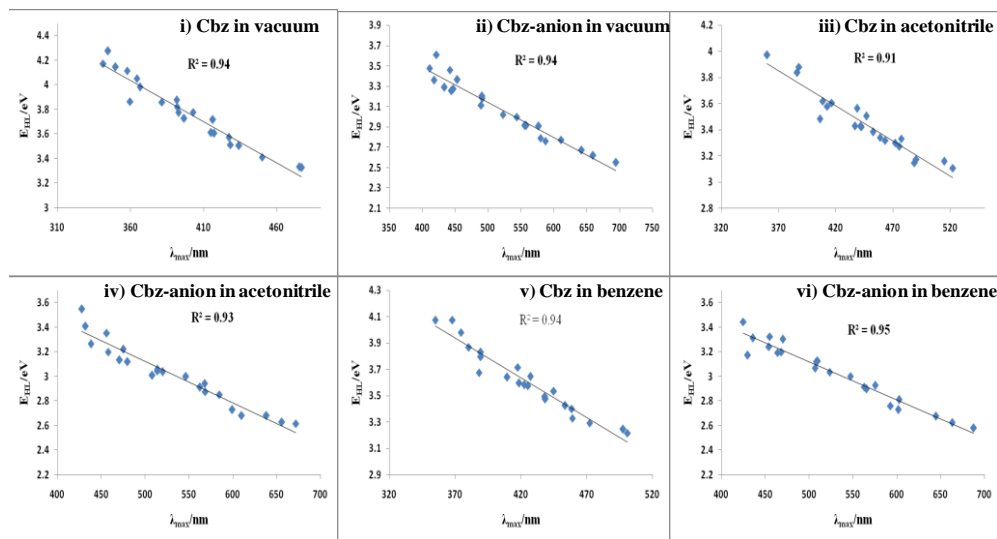


Fig. 4. Graph of longest λ_{max} vs. HOMO-LUMO energy gap of doubly substituted carbazole (Cbz) in (i) vacuum, (iii) acetonitrile, (v) benzene and carbazole-anion (Cbz-anion) in (ii) vacuum, (iv) acetonitrile, (vi) benzene. (See Table 2)

and C5 positions to the Cbz the λ_{\max} shifts from 290.56 to 477.15 nm. However, for the Cbz-anion, substitution of NH₂ at C4 and NO₂ at C5 position shifts the λ_{\max} from 361.98 to 694.61 nm. Similar red shift in λ_{\max} is also observed in acetonitrile and benzene solvents. A good correlation of HOMO-LUMO energy gap with λ_{\max} having correlation coefficient 0.94 highlights the dominance of intramolecular charge transfer from NH₂ to NO₂ group through Cbz moieties. Present QSPR study can provide valuable insights for attaching donating and withdrawing groups at the suitable sites of the Cbz and its anionic form for designing of photosensitizer for an efficient DSSC and other optoelectronic properties.

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Supporting informations

Informations of about longest maximum absorption wavelengths, Oscillator strength, HOMO-LUMO energy gap of substituted Cbz by NH₂ and NO₂ at its Nitrogen site are available from VBRI Press.

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