RESEARCH ARTICLE



Combined experimental and density functional theory studies on novel 9-(4/3/2-cyanophenyl)-9H-carbazole-3-carbonitrile compounds for organic electronics

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Abstract

We have synthesized a series of novel hybrid molecules 9-(2-cyanophenyl)-9H-carbazole-3-carbonitrile (o-CNCbzCN), 9-(3-cyanophenyl)-9H-carbazole-3-carbonitrile (m-CNCbzCN) and 9-(4-cyanophenyl)-9H-carbazole-3-carbonitrile (p-CNCbzCN), comprising electron-donating carbazole and electron-accepting nitrile groups. Three positional isomers were synthesized with a view to tune photophysical and electrochemical properties of the hybrids. The photophysical study displayed absorption maxima in the range of 281-340 nm and 277-298 nm whereas emission maxima in the range of 349-366 nm and 366-369 nm in toluene and dimethylformamide (DMF), respectively. These molecules demonstrated suitable frontier molecular orbital (FMO) energy levels and ensure good thermal and morphological stability. Among these synthesized molecules, *m*-CNCbzCN showed very high decomposition temperature ($T_d = 341^{\circ}$ C) whereas *p***-CNCbzCN** exhibited good glass transition ($T_g = 182^{\circ}C$) as well as melting temperature ($T_{\rm m} = 236^{\circ}$ C), indicating its significant stability and potential utility as a bipolar host material for efficient phosphorescent organic light-emitting diodes (PhOLEDs).

KEYWORDS

carbazole, carbonitrile, density functional theory, donor-acceptor system, photophysical study

advantage of these organic semiconductor materials is low cost, lightweight, and possibility of producing flexible

and great area devices which make them the best substituents for inorganic semiconductor materials.^[7-10] Among

INTRODUCTION 1

Over the past few decades, an intense research effort has been made for the design, synthesis, and application of organic materials. At the present time, these organic materials are emerging as the best alternative for inorganic semiconductor materials and found applications in organic light-emitting diodes (OLEDs),^[1,2] organic photovoltaics (OPVs),^[3,4] dye-sensitized solar cells (DSSCs),^[5] and organic thin-film transistors (OTFTs).^[6] A further

above stated optoelectronic devices, an OLED-based flexible flat panel display has already conquered the markets in the form of digital cameras, television, and cell phones.^[11-15] Nevertheless, phosphorescent OLEDs (PhOLED) are promising owing to their ability to achieve 100% internal quantum efficiency. In these devices phosphorescent metal-complex emitters are commonly doped into a suitable bipolar host material in order to reduce concentration quenching and triplet-triplet annihilation. The bipolar materials with donor-acceptor (D-A) system comprising π or σ bridge have engaged with great significance because of their distinctive properties like well-defined structural system, balance hole and electron transport, ease of purification along with authentic reproducibility, high luminescence quantum yield,^[16-18] and easy fabrication of large area devices.^[19-27] Over a wide range of tailored D-A moieties along with unique architecture system with wise selection and proper linking of donor and acceptor motifs allows to tune the photophysical, thermal, and electrochemical properties.^[28] Indeed, a host material for PhO-LEDs device should possess some inherent features: (I) higher triplet energy $(E_{\rm T})$ than the phosphorescent guest, which prevent reverse energy transfer, (II) suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for effective charge injections into the emitting layer from the adjacent charge transporting layers, (III) large HOMO-LUMO energy gap (E_{α}) than the phosphorescent guest, and (IV) high glass transition temperature (T_g) to provide good film morphology and avoid morphological changes at device operating voltage and so on.

Unlike unipolar host, bipolar hosts promote balance holes and electrons mobility which leads to generation of broad charge recombination zone and eventually alters the device structure; this results into augmentation of the device performance.^[29-34] In this context, diverse D-A molecules consist of high triplet energy $(E_{\rm T})$ donors such as triphenylamine,^[35-37] carbazole,^[38-40] dibenzothiophene,^[41] and dibenzofuran^[42,43] and acceptors such as oxadiazole, triazole, azine, phenanthroline, and benzimidazole have been synthesized and successfully used in the device fabrication. Indeed, carbazole exhibit several meritorious properties like high triplet energy level, small conjugated system, and chemical stability, which made it as favorable donor moiety in synthesis of bipolar materials.^[44-46] Hitherto, cvano (-CN)-containing compounds are not so extensively studied as bipolar host materials for PhOLEDs. It was noted that the strong electron-withdrawing cyano group (-CN) should be a good candidate as n-type unit to form D-A host molecules.^[47–49] Lin and coworkers used a typical -CN group to decorate the well-known benchmark blue host material mCP (N,N-dicarbazolyl-3,5-benzene) and realized the excellent device results.^[47] Recently, two novel host materials CNPhCz and DCNPhCz comprehending carbazole and cyanophenyl units were designed, synthesized, and fully characterized by Liu et al. and Li et al.. CNPhCz-hosted blue and green devices exhibited maximum external quantum efficiencies of 17.1 % and 24.4 %, respectively with significantly small efficiency roll-off.^[50,51] Li and coworkers reported three positional isomers *o*-CzCN, *m*-CzCN, and *p*-CzCN with donor:acceptor ratio of 2:1. *m*-CzCN-hosted blue phosphorescent OLED exhibited an external quantum efficiency of 23.14% with a maximum current efficiency of 46.81 cd A^{-1} .^[52]

Herein, we report the synthesis of three novel D-A materials 9-(2-cyanophenyl)-9H-carbazole-3-carbonitrile (o-CNCbzCN), 9-(3-cyanophenyl)-9H-carbazole-3carbonitrile (*m*-CNCbzCN), and 9-(4-cyanophenyl)-9H-carbazole-3-carbonitrile (p-CNCbzCN) by using a combination of carbazole core as donor unit with peripheral cyano (-CN) as an acceptor unit encompassing ratio of 1:2 (shown in Scheme 1). This investigation shed a light on effect of position of CN group on properties of molecules such as photophysical, electrochemical, and intramolecular charge transfer (ICT), HOMO-LUMO energy levels, and energy band gap. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies are also performed to support experimental findings. Additionally, calculated charge transport parameters such as ionization potential, electron affinity, and reorganization energies of synthesized molecules are also reported.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

Chemical reagents were purchased from commercial suppliers. All reactions were done in a round bottom flask and monitored by TLC performed on aluminum plates (0.25 mm, E. Merck) precoated with silica gel (Merck 60 F-254). Developed TLC plates were visualized under a short-wavelength UV lamp. Reactions were conducted an open-air atmosphere in solvent such as dimethylformamide (DMF). Yields refer to spectroscopically (¹H and ¹³C NMR) homogeneous material obtained after column chromatography performed on silica gel (100-200 mesh size) supplied by S.D. Fine Chemicals Limited, India. ¹H and ¹³C NMR were recorded in DMSO solution with a Bruker 300-MHz spectrometer. Chemical shifts (δ) are quoted in ppm, relative to SiMe₄ ($\delta = 0.0$) as an internal standard. The number of protons (n) for a given resonance is indicated by nH. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; and J, coupling constant in Hz. High-resolution mass spectra (HRMS) were obtained by using positive electrospray



SCHEME 1 Synthetic routes for bipolar host materials *p*-CNCbzCN, *m*-CNCbzCN, and *o*-CNCbzCN

ionization (ESI) by time-of-flight (TOF) method. Melting points were recorded on a standard melting point apparatus from Gautam Lab Equipment, Mumbai, and are uncorrected. Electronic absorption spectra were recorded on UV-Vis-NIR spectrophotometer. Emission spectra were recorded on Varian Cary-Eclipse fluorescence spectrophotometer. The thermal properties were measured on Mettler Toledo system with a heating rate of 20°C/min and N₂ flow of 20 ml/min. Electrochemical studies were performed using Metrohm potentiostat/ galvanostat Autolab PGSTAT 100 with a scan rate of 100 mV/s. A standard three-electrode cell comprising Ag/AgCl, a platinum wire, and a glassy carbon electrode as the reference, counter, and working electrodes, respectively, was used. HOMO is calculated from the oxidation peak potentials.

2.2 | General procedure for the synthesis of 9-(4/3/2-cyanophenyl)-9*H*-carbazole-3-carbonitrile (6/11/16)

A round bottom flask containing mixture of 4/3/2-(3-bromo-9*H*-carbazol-9-yl) benzonitrile (**5/10/15**)

(0.5 g, 1.44 mmol) and CuCN (0.19 g, 2.12 mmol) were dissolved in N,N'-DMF (5 ml). After stirring for 24 h, reaction mixture was allowed to cool at room temperature. After completion of reaction (as indicated by TLC Rf: 0.7), 60 ml of aqueous ammonia and 60 ml of water were added, and the reaction mixture was extracted with dichloromethane (2 × 50 ml). The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under vacuum. Crude solid obtained was then purified by silica gel column chromatography with hexane:ethyl acetate (80:20).

2.2.1 | 9-(4-Cyanophenyl)-9*H*-carbazole-3-carbonitrile (6)

Pale yellow solid. Yield. 80% (0.33 g). ¹H NMR (300 MHz, DMSO, ppm): δ 8.96–8.87 (m, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 2H), 7.93–7.74 (m, 3H), 7.57–7.38 (m, 4H); ¹³C NMR (75 MHz, DMSO, ppm): 166.9, 141.6, 140.6, 138.2, 133.8, 129.5, 127.7, 126.5, 125.8, 123.2, 121.9, 121.5, 120.0, 110.8, 110.2, 102.1. HRMS-ESI (*m*/*z*): calcd for C₂₀H₁₁N₃, [M + H]⁺: 293.0953; found, 293.0955.

2.2.2 | 9-(3-Cyanophenyl)-9*H*-carbazole-3-carbonitrile (11)

Pale yellow solid. Yield. 76% (0.32 g). ¹H NMR (300 MHz, DMSO, ppm): δ 8.88 (s, 1H), 8.53 (s, 1H), 8.40–8.31 (m, 1H), 8.15–8.04 (m, 2H), 7.81–7.79 (m, 2H), 7.58–7.33 (m, 4H); ¹³C NMR (75 MHz, DMSO, ppm): 166.7, 141.9, 140.8, 136.4, 135.8, 130.4, 129.5, 127.7, 127.1, 125.7, 123.0, 121.7, 121.3, 120.6, 120.0, 112.2, 111.6, 110.8, 110.2, 101.9; HRMS-ESI (*m*/*z*): calcd for C₂₀H₁₁N₃, [M + H]⁺: 293.0953; found, 293.0952.

2.2.3 | 9-(2-Cyanophenyl)-9*H*-carbazole-3-carbonitrile (16)

Pale yellow solid. Yield. 72% (0.30 g). ¹H NMR (300 MHz, DMSO, ppm): δ 8.95–8.81 (m, 1H), 8.65–8.52 (m, 1H), 8.40–8.30 (m, 1H), 8.16–8.05 (m, 2H), 7.88–7.79 (m, 2H), 7.57–7.32 (m, 4H); ¹³C NMR (75 MHz, DMSO, ppm): 166.8, 140.4, 138.8, 136.4, 130.3, 129.5, 128.7, 127.5, 127.1, 125.5, 124.7, 123.7, 123.1, 121.3, 120.6, 112.2, 111.6, 110.8, 109.8, 101.9. HRMS-ESI (*m*/*z*): calcd for C₂₀H₁₁N₃, [M + H]⁺: 293.0953; found, 293.0956.

3 | **RESULTS AND DISCUSSION**

3.1 | Synthesis

The intermediates 9-(4-bromophenyl)-9*H*-carbazole (**3**), 9-(3-bromophenyl)-9*H*-carbazole (**8**), and 9-(2-bromophenyl)-9*H*-carbazole (**13**) were prepared in good yields from carbazole using Ullmann coupling reaction.^[53–56] These intermediates were then converted to 4-(9*H*-carbazol-9-yl)benzonitrile (**4**), 3-(9*H*-carbazol-9-yl)benzonitrile (**9**), and 2-(9*H*-carbazol-9-yl)benzonitrile(**14**) by replacing bromo group by cyano group using copper cyanide. Subsequently, intermediate **4**, **9**, and **14** were brominated at C3 position of carbazole which eventually converted to **o-CNCbzCN**, **m-CNCbzCN**, and **p-CNCbzCN** using copper cyanide. These compounds were confirmed by ¹H and ¹³C NMR spectroscopy and high-resolution mass analysis.

3.2 | Thermal properties

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to probe the thermal properties of o-CNCbzCN (16), m-CNCbzCN (11), and p-CNCbzCN (6) at a heating rate of 20°C/min under a nitrogen flow. Earlier reported cyano derivatives by Lin et al. (mCPN and mCP),^[47] Zhang et al. (CBP-CN and CBP),^[48] and Liu et al. and Li et al. (*m*-PyCNmCP, 3-PyCNmCP, CNPhCz, and DCNPhCz)^[50,51] exhibited glass transition temperatures in the range of 49°C to 162° C and decomposition temperature (T_{d}) in the range of 280°C to 440°C. However, our molecules o-CNCbzCN, m-CNCbzCN, and p-CNCbzCN showed distinctly higher glass transition temperatures $(131^{\circ}C \text{ to } 182^{\circ}C)$ and decomposition temperatures (T_d) in the range of 338°C to 341°C. The high $T_{\rm g}$ values are observed due to encapsulation of two -CN groups on N-phenyl carbazole molecule. In addition, melting temperature of *m*-CNCbzCN and *p*-CNCbzCN is found at 212°C and 236°C, respectively (Figure 1 and Table 1). The significantly high glass transition temperature (T_g) and



FIGURE 1 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of *o*-CNCbzCN, *m*-CNCbzCN, and *p*-CNCbzCN recorded at a heating rate of 20°C/min

Molecule	λ _{abs.} ^[a] (nm) DCM	λ _{fluor.} ^[b] (nm) DCM	HOMO (eV)	LUMO ^[c] (eV)	E _{oxi} ^[d] (V)	E _{red} ^[e] (V)	$T_{\rm d}^{\rm [f]}/T_{\rm m}^{\rm [g]}/T_{\rm g}^{\rm [h]}$ (°C)
o-CNCbzCN	274	353, 363	-6.19	-2.21	1.84	-0.43	337.7/-/167.7
m-CNCbzCN	275	350, 366	-6.29	-2.29	1.94	-0.40	341.5/212/131.3
p-CNCbzCN	274	351, 367	-6.32	-2.76	1.97	-0.49	338.7/236/181.6

TABLE 1 Photophysical, thermal, and electrochemical data of the synthesized molecules

Abbreviations: LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital.

^aAbsorption maximum.

^bFluorescence maximum.

^cLUMO levels were derived via eq. LUMO = HOMO + E_g .

 ${}^{d}E_{\text{oxi}}$, oxidation peak potential (V).

 $^{e}E_{red}$, reduction peak potential (V).

 ${}^{\rm f}T_{\rm d},$ thermal decomposition temperature.

 ${}^{\mathrm{g}}T_{\mathrm{m}},$ melting temperature.

 ${}^{\rm h}T_{\rm g}$, glass transition temperature.

decomposition temperature (T_d) values of our host materials imply its capability for enduring stable amorphous thin films through vacuum thermal sublimation and suppress aggregation formation.

3.3 | Photophysical properties

Electronic absorption and photoluminescence (PL) spectra (recorded at room temperature) of *p*-CNCbzCN, *m*-CNCbzCN, and *o*-CNCbzCN in various solvents are depicted in Figure 2, and respective data are summarized in Table 1.

Figure 2 displays UV-Vis and PL spectra of o-CNCbzCN, m-CNCbzCN, and p-CNCbzCN in various solvents. Previous reports on cyano derivatives by Lin et al. (mCPN and mCP),^[47] Zhang et al. (CBP-CN and CBP),^[48] and Liu et al. and Li et al. (*m*-PyCNmCP, 3-PyCNmCP, CNPhCz, and DCNPhCz)^[50,51] exhibited UV absorbance maxima in the range of 284-339 nm and emission maxima in the range of 346-434 nm. However, our molecules o-CNCbzCN, m-CNCbzCN, and *p***-CNCbzCN** showed absorption maxima in the range of 274-275 nm and emission maxima in the range of 350-367 nm (Table 1). In the UV-Vis spectra of o-CNCbzCN, m-CNCbzCN, and p-CNCbzCN, the solvent polarity-independent absorption peaks around 257 nm are ascribed to the π - π * transition.^[57-59] The absorption spectra of these three compounds measured in cyclohexane, toluene, CH2Cl2, MeCN, and DMF showed nearly similar absorption properties. Such solvent-independent absorption spectra suggest that the Franck-Condon excited states are subjected to rather small changes in dipole moment with respect to the ground states. The PL spectra of o-CNCbzCN, m-CNCbzCN, and p-CNCbzCN illustrated prominent solvent-dependent emission properties. As the solvent

polarity increases, bathochromic shifts were observed in their PL spectra of all the three compounds, which could be due to the strong ICT character at the excited state. On comparing with the UV-Vis absorption spectra, all the three compounds showed larger Stokes shifts in different solutions, which also means that all of them have ICT character. The gradual red shifted emission suggests rapid photoinduced electron transfer (PET) within the D-A moiety. Due to PET, dipole moment of excited state changes significantly which could be stabilized by dielectric environment. The HOMO–LUMO gap, that is, band gap is estimated from the Tauc plot (refer to the Supporting Information) (Table 2).

3.4 | Electrochemical properties

The electrochemical behavior particularly band structure parameters of o-CNCbzCN, m-CNCbzCN, and *p*-CNCbzCN were investigated by using cvclic voltammetry (CV) method. Three-electrode cell system encompassing a glassy carbon as working electrode, silver/silver chloride (Ag/AgCl) as reference electrode, and a platinum wire as counter electrode was used. A ferrocene (Fc) was used as an internal standard for CV. The CV experimental measurements are included in Section 2, and the result is summarized in Figure 3 and Table 1, where tetra(n-butyl)ammonium hexafluorophosphate (TBAPF₆) in CH_2Cl_2 as a supporting electrolyte (0.1 M) was used for the oxidation scans.^[60]

All the three compounds **o-CNCbzCN**, *m***-CNCbzCN**, and *p***-CNCbzCN** exhibited an irreversible oxidation peak potential. The oxidation onsets of **o-CNCbzCN**, *m***-CNCbzCN**, and *p***-CNCbzCN** observed at 1.84, 1.94, and 1.97 V (vs. Ag/AgCl), respectively. It was worthy to note that **o-CNCbzCN** and *m***-CNCbzCN** exhibited nearly the same oxidation peak potential value



2.34

2.46

4.16

4.16

TABLE 2Calculated band gap (ineV) from Tauc plot, cyclic voltammetry,and DFT study

Abbreviations: CV, cyclic voltammetry; DFT, density functional theory.

4.00

3.56

m-CNCbzCN

p-CNCbzCN

which correlates to the degree of π -conjugation due to 9*H*-phenyl carbazole moiety. HOMO energy level was calculated using formula HOMO (eV) = $-(E_{\text{oxonset}} - E_{\text{Fc/Fc+onset}}) - 4.80 \text{ eV}$ and those appear at -6.19, -6.29, and -6.32 for **o-CNCbzCN**, **m-CNCbzCN**, and **p-CNCbzCN**, respectively (Table 2). LUMO energy levels were calculated from the HOMO energy levels using the equation LUMO = HOMO + E_{g} , where E_{g} is absorption wavelength band gap, that is, -2.21, -2.29,

and -2.76 for **o-CNCbzCN**, **m-CNCbzCN**, and **p-CNCbzCN**, respectively.

To get more insight into absorption properties, quantum mechanical calculations are performed for these reported molecules. The electronic ground-state geometries of all the three molecules are fully optimized in gas phase without any symmetric considerations by using Becke's three-parameter hybrid exchange with the Lee–Yang–Parr correlation functional (B3LYP) with a 6-31G(d,p) basis set. Vibrational frequencies were evaluated for the optimized geometries at the same level of calculations to ensure that the structure obtained was



FIGURE 3 Cyclic voltammograms of *o*-CNCbzCN, *m*-CNCbzCN, and *p*-CNCbzCN

a minimum on the potential energy surface. To predict the absorption maxima, vertical excitation energies were calculated with TDDFT method at the CAM-B3LYP/6-31G(d,p) level. All the calculations were carried out using ab initio software Gaussian 09W program.^[61]

To get absorption energies of the molecules, TDDFT calculations have been carried out for the molecules under study. The calculated absorption energies are in good agreement with the experiment and are having absorption maxima in the range of 281 to 291 nm. Calculated lowest three states absorption energies (S1, S2, and S3), oscillator strength, major transitions along with percentage weight are shown in Table 3a. The first excitation (S1) in *o*-CNCbzCN and *p*-CNCbzCN molecules is due to the major transition from HOMO to LUMO, whereas *m*-CNCbzCN is due the transition between HOMO to LUMO + 1, and corresponding molecular orbitals are shown in Figure 4.

It is evident from Figure 4. That HOMO is localized on backbone of the molecule whereas its LUMO is dispersed on the benzene ring with CN group as substitution at *ortho*, *meta*, and *para* positions. This indicates that these molecules are exhibiting D-A-type charge transfer character.

The calculated HOMO and LUMO energies are following the experimental trend and the HOMO–LUMO gap calculated from DFT are in excellent agreement with HOMO–LUMO gap estimated from the CV and

TABLE 3a Absorption energies (λ_{max} in nm), oscillator strength (f), major transitions (MT), % weight (% C_i) obtained at TD-CAM-B3LYP method

Molecule	State	$\lambda_{ ext{max}}$	f	МТ	% <i>C</i> _i
o-CNCbzCN	S1	291	0.075	$H \to L$	89
	S2	278	0.018	$H-1 \rightarrow L+3$	14
				$H \to L \textbf{+} 1$	71
	S3	260	0.024	$H-1 \rightarrow L+1$	50
				$H \to L + 2$	20
				$H \to L \textbf{+} \textbf{3}$	16
m-CNCbzCN	S1	281	0.035	$H \to L \textbf{+} 1$	76
				$H-1 \rightarrow L+3$	11
	S2	277	0.053	$H \to L$	86
	S3	262	0.062	$H-1 \rightarrow L+1$	32
				$H \to L + 2$	50
p-CNCbzCN	S1	284	0.361	$H \to L$	77
				$H \to L \textbf{+} 1$	11
	S2	281	0.023	$H \to L$	15
				$H \to L \textbf{+} 1$	67
	S3	259		$H-1 \rightarrow L+1$	58
				$H \to L + 3$	23

Note: % weight (% C_i), weight more than 10% indicated in the table.



FIGURE 4 Molecular orbital pictures of synthesized molecules

TABLE 3b Calculated HOMO energy, LUMO energy, HOMO–LUMO gap (HLG in eV), and ground-state (μ_g) and excited-state (μ_e) dipole moments (in Debye) obtained at B3LYP method

Molecule	номо	LUMO	HLG	$\mu_{ m g}$	μ_{e}
o-CNCbzCN	-6.03	-1.96	4.07	8.13	9.35
m-CNCbzCN	-6.12	-1.96	4.16	4.62	6.78
p-CNCbzCN	-6.15	-1.99	4.16	4.18	4.39

UV-Vis spectroscopy experimentally. The calculated dipole moment of excited molecule changes significantly which could be stabilized by dielectric environment (Table 3b).

The geometrical inequality between ground (S0) and excited (S1) states in the dihedral angles of **o-CNCbzCN**, *m***-CNCbzCN**, and *p***-CNCbzCN** are apparent from Table 4. In **o-CNCbzCN**, dihedral angle increased from -68.35° to -90.91° , whereas in *m***-CNCbzCN**, dihedral angle increased from -56.42° to -87.94° . On the other hand, in *p***-CNCbzCN**, the same was increased from -53.59° to 88.89° . The above outcomes specify that the molecular configuration of carbazole and cyanophenyl in all the three molecules is twisted in S1 state and the angle of twisting in between S1 and S0 varies significantly, which concur with the donor to acceptor charge transfer behavior in these molecules.

The dihedral angles obtained from B3LYP/6-31G(d,p) S0 and TD-B3LYP/6-31G(d,p) S1 geometries of **o-CNCbzCN**, **m-CNCbzCN**, and **p-CNCbzCN** are shown in Table 4.

3.5 | Charge transport and charge injection parameter of the synthesized molecules

According to hopping model, charge transfer reaction is self-exchange electron transfer reaction between neutral and radical cation (hole transfer) shown in Equation 1:

$$M + M^+ \to M^+ + M. \tag{1}$$

Marcus expresses the rate constant (*K*) for charge transfer reaction between two molecules shown in Equation $2 \text{ as}^{[62,63]}$

$$K = \left(\frac{4\pi^2}{h}\right) H^2 (4\pi\lambda kT)^{-1/2} \exp(-\lambda/_{4kT}).$$
(2)

Here, *H* is charge transfer integral matrix between neighboring molecules,^[64,65] λ is reorganization energy, *k* is Boltzmann constant, and *T* is the temperature. Total reorganization energy is the sum of internal and external

TABLE 4 Ground- and excited-state optimized geometries



reorganization energies; however, external λ is negligible as compared with internal λ .^[66] The calculation of internal λ is done by using the following equations.

$$\lambda_{\rm h} = \lambda_1 + \lambda_2 = [E^+(M_0) - E^+(M_+)] + [E^0(M_+) - E^0(M_0)],$$
(3)

$$\lambda_{\rm e} = \lambda_3 + \lambda_4 = [E^-(M_0) - E^-(M_-)] + [E^0(M_-) - E^0(M_0)].$$
(4)

Calculation of ionization potentials (adiabatic $[IP_a]$ and vertical $[IP_v]$) and electron affinities (adiabatic $[EA_a]$ and vertical $[EA_v]$) are done by Equations (5) and (6), respectively, as they are important parameter regarding charge injection phenomenon.

$$IP_{a} = E^{+}(M_{+}) - E^{0}(M_{0}), \qquad (5a)$$

$$IP_{\rm v} = E^+ (M_0) - E^0 (M_0), \qquad (5b)$$

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Name	IPa	IP _v	EA _a	EA_{v}	$\lambda_{\mathbf{h}}$	$\lambda_{\mathbf{e}}$	E _{S-T}
o-CNCbzCN	7.43	7.49	0.49	0.35	119	290	3.19
m-CNCbzCN	7.50	7.55	0.49	0.37	90	252	3.19
p-CNCbzCN	7.52	7.56	0.58	0.46	81	241	3.16

TABLE 5 Calculated ionization potential (*IP*, in eV), electron affinity (*EA*, in eV), hole and electron (λ_h and λ_e) reorganization energy (in meV), and singlet-triplet gap (E_{S-T} in eV)

$$EA_{a} = E^{0}(M_{0}) - E^{-}(M_{-}), \qquad (6a)$$

$$EA_{\rm v} = E^0(M_0) - E^-(M_0). \tag{6b}$$

Here, in the above equations, $E^+(M_0)/E^-(M_0)$ is the energy of cation/anion obtained at ground-state neutral molecule, and $E^0(M_+)/E^0(M_-)$ is the energy of neutral molecule obtained at optimized cationic/anionic state. The lowest energies of cation, anion, and neutral state are represented by $E^+(M_+)$, $E^-(M_-)$, and $E^0(M_0)$, respectively.

The calculation of IP and EA is carried out for the reported molecules, as they are responsible for energy barrier regarding injection of the holes and electrons, respectively. IP is defined as the energy required to remove an electron, and it must be sufficiently low for efficient hole injection into the HOMO of the molecule. The smaller IP of the hole-transport layer (HTL), the easier will be the injection of holes from indium tin oxide (ITO) to HTL. EA is defined as the energy released when an electron is added to the system, and it must be high enough to allow an efficient electron injection into LUMO of the molecule. The EAa (EAv) values are higher for the molecule p-CNCbzCN among all the molecules, suggesting there is efficient electron injection in LUMO level of this molecule. ^[67,68] In Table 5, calculated values of IP and EA are tabulated. From Table 5, it is observed that the calculated IP_a (IP_v) values for ortho-substituted molecule is 7.43 eV (7.49 eV) and is smallest among all the isomers. Hence, it is easy to create a hole in orthosubstituted molecule compared to para- and metasubstituted isomers.

The calculated hole (λ_h) and electron (λ_e) reorganization energy for *ortho-*, *meta-*, and *para-*substituted molecule are shown in Table 5. As evident from Equation 2, smaller reorganization energy leads to the higher rate constant value which in turn increases the charge transport properties in the molecule. From Table 5, *para-*substituted isomer is showing smallest λ_h value of 81 meV, whereas *meta-* and *ortho-*substituted isomers are showing 90 and 119 meV, respectively. Similar is the case for λ_e values, *para* isomers is showing smallest (241 meV) and *ortho* being the highest (290 meV). Moreover in all

the molecules, $\lambda_{\rm h} < \lambda_{\rm e}$, suggesting that the studied molecules are better candidates as hole-transporting materials. Also, the λ_h calculated for the isomers are smaller than that of *N*,*N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) which is typical hole-transport material ($\lambda_{\rm h} = 290$ meV).^[69] Furthermore, the λ_e calculated for the isomers are smaller than tris (8-hydroxyquinolinato)aluminum(III) (Alq3) which is considered as typical electron-transport material $(\lambda_e = 276 \text{ meV}).^{[70]}$ In conclusion, the theoretical shows that the studied isomers are showing smaller reorganization energy than standard molecule reported in literature. Also, the synthesized isomers are showing very small hole reorganization energy suggesting these isomers are better candidate for hole-transport materials.

To know singlet-triplet gap ($E_{\text{S-T}}$ in eV), the molecules are also optimized in their triplet state, calculated ($E_{\text{S-T}}$) are tabulated in Table 5 using Equation 7. From Table 5, it is clear that the singlet-triplet gap energies are in the range of 3.16–3.19 eV. This showed that these could be potential bipolar host materials for realization of phosphorescent LEDs.

$$E_{\rm S-T} = E_{\rm triplet} - E_{\rm singlet}.$$
 (7)

4 | CONCLUSIONS

A series of dicyano derivatives of *N*-phenyl carbazole was synthesized via Ullmann coupling reaction and other synthetic methods. The absorption, emission, thermal, and electrochemical properties as well as DFT studies of the synthesized materials were reported. The properties of the molecules are significantly influenced by the position of the cyano segment attached to the phenyl ring of *N*-phenyl carbazole. The HOMO energy levels of these three compounds were found in the range of -6.19 to -6.32 eV and were comparable with those of the commonly used hole-transporting materials. Experimental data are in correlation with the theoretical data calculated by DFT and TDDFT methods. The thermal study showed that these derivatives have high glass transition temperature and good thermal stability. The results obtained for the HOMO–LUMO positions and the energy gap from DFT calculation show very close agreement with the experimentally estimated values using spectroscopy and CV. Lastly, on the basis of the theoretical and experimental study, we believe that these compounds have the potential to be used as bipolar host materials in optoelectronic device fabrication.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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