#### **ORIGINAL ARTICLE**



# Photophysical and Electrochemical Properties of Highly $\pi$ -Conjugated Bipolar Carbazole-1,3,4-Oxadiazole-based D- $\pi$ -A Type of Efficient Deep Blue Fluorescent Dye

Mahesh Sadashivappa Najare<sup>1</sup> · Mallikarjun Kalagouda Patil<sup>2</sup> · Tarimakki Shankar Tilakraj<sup>2</sup> · Mohammed Yaseen<sup>1</sup> · AfraQuasar A Nadaf<sup>1</sup> · Shivaraj Mantur<sup>1</sup> · Sanjeev Ramchandra Inamdar<sup>2</sup> · Imtiyaz Ahmed M Khazi<sup>1</sup>

Received: 17 May 2021 / Accepted: 5 July 2021 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

#### Abstract

In this contribution, we have designed and synthesized a novel carbazole-1,3,4-oxadiazole based bipolar fluorophore (E)-2-(4-(4-(9H-carbazol-9-yl)styryl)phenyl)-5-(4-(tertbutyl) phenyl)-1,3,4-oxadiazole (CBZ-OXA-IV). Wittig reaction is utilised for the synthesis of the designed bipolar target compound CBZ-OXA-IV. <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and ESI-MS results confirmed the designed chemical structure of the fluorophore CBZ-OXA-IV. The photophysical properties have been investigated in detail using UV-Vis absorption, photoluminescence spectroscopy. Also, the photoluminescence studies on solid state samples (as thin films) were carried out. The CBZ-OXA-IV dye emits intense deep blue fluorescence with observed absorption and emission maxima occurring are at 353 nm and 470 nm, respectively. Fluorophore CBZ-OXA-IV has shown high Stokes shift of 7052 cm<sup>-1</sup>. The experimentally measured optical band gap  $(E_{q}^{opt})$  value is found to be 3.01 eV and the fluorescence quantum yields ( $\Phi_f$ ) is 0.40. The intramolecular charge transfer property of **CBZ-OXA-IV** dye was examined by using photophysical properties such as absorption, emission in different solvents of different varying polarities. In addition, Density Functional Theory computations are studied in detail including the MEP surface plots and natural bond orbital analysis. The electrochemical properties have been investigated in detail by using cyclic voltammetry measurements. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement results display a high thermal stability with decomposition temperature ( $T_{d5\%}$ ) 387 °C and a large glass transition temperature ( $T_g$ ) of 98 °C. The obtained results demonstrated that the novel bipolar fluorophore CBZ-OXA-IV could play an important role in organic optoelectronics and possibly can be utilized as bipolar transport materials for electroluminescence applications in optoelectronic devices/OLEDs.

**Keywords** Photophysical properties  $\cdot$  Bipolar fluorophore  $\cdot$  Carbazole  $\cdot$  1,3,4-Oxadiazole  $\cdot$  Electrochemical properties  $\cdot$  DFT Computations

# Introduction

During the last three decades enormous research has been dedicated to the field of optoelectronics, including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), sensors, organic solar cells (OSCs) and photovoltaics [1]. Since the invention of organic light-emitting diodes (OLEDs), first introduced by Tang and VanSlyke in 1987, OLEDs are considered as one of the most promising technologies, due to their promising properties and numerous advantages such as light weight, rapid response, wide-viewing angles, low driving voltage, high brightness, color-purity, high optical transparency and the possibility for fabrication into large and flexible displays [2–6]. There-fore, OLEDs have attracted immense attention in academic, scientific and industrial areas for their potential applications as ecofriendly candidates for the next-generation full-color flat panel displays and solid-state lighting sources [7–9]. The simplest architecture of multilayer OLEDs comprise of an anode, a hole transporting material (HTM) layer, emissive material layer (EML), an electron transporting material

Mahesh Sadashivappa Najare mahesh.s.najare@gmail.com

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, Karnatak University, Dharwad 580003, Karnataka, India

<sup>&</sup>lt;sup>2</sup> Laser Spectroscopy Programme, Department of Physics, UGC-CPEPA, Karnatak University, Dharwad 580003, Karnataka, India

(ETM) layer and a cathode [4, 10]. The general working principle of an OLED devices is, when a voltage is applied across the two electrodes, then charges (holes from the anode and electrons from the cathode) are injected in the organic material. Then, the charges move inside the material, and recombine to form excitons. A photon is emitted when the exciton recombines [11]. Despite the advancements in the field of OLEDs, the development of efficient and stable OLEDs for their practical use into large-scale commercial applications, still have some unresolved problems such as high production cost, high power consumption, low efficiency and lifetime [12, 13]. Organic emitting materials with low thermal decomposition temperature (Td) or low glass transition temperature (Tg) may result in the faster degradation of organic devices due to morphological changes leads to the lower lifetime of the devices [14]. Further, the performance of blue and deep blue OLEDs is in fact not good enough, in terms of their lower efficiency and stability, which are extensively dependent on the blue luminescent organic materials [15]. In order to address these drawbacks, a new class of organic materials should be synthesized as organic light-emitting materials. Among all the possible organic materials, small  $\pi$ -conjugated organic molecules are most extensively used. Due to their various advantages such as easy, tunable and reproducible synthesis along with simple purification protocols [7]. Over the past two decades, the organic materials with donor- $\pi$ -acceptor (D- $\pi$ -A) form are accepted as one of the most promising strategies for improving OLEDs performance [16]. They have received overwhelming importance as electroluminescent materials for organic electronics, particularly for energy consumption and energy harvesting devices, such as organic light-emitting devices [17]. An extensively used strategy for design OLED over the past year is to introduction of electron-rich donors or electron-deficient acceptors to a suitable organic core structure to get hole transporting or electron transporting materials, respectively [18]. A major drawback in this device structure is the imbalance of charge-transporting character of organic materials when only electron-transport or hole-transport materials are used as it gives rise to low device efficiency and reduced lifetime [18]. Effective control of charge balance is essential for high performance OLED devices [19]. This can be achieved by the synthesis of new organic materials possessing bipolar properties. Which is the combination of both the electron donating (D) and electronaccepting (A) moieties within a single molecule, the resulting bipolar materials provide the background for a good balance between electron and hole mobilities (charge balance), resulting in the broadening of exciton recombination zones [20–22]. This constitutes one of the mandatory conditions for the fabrication of single-layer material and consequentially, to give high efficiency organic light-emitting diodes (OLEDs) and low efficiency roll-off [21]. The devices with bipolar fluorophores are easier to fabricate and the manufacturing costs are reduced [23]. Organic fluorophores with comparable hole- and electron-transporting abilities are also termed ambipolar molecules [23].

In view of the above mentioned points, carbazole is a known popular heterocyclic moiety, widely used as a electron donor component for optoelectronic materials [23] due to their excellent optical property and ease of functionalization. Carbazole derivatives have been extensively used as host organic materials for multiple optoelectronic and photovoltaic applications such as in OLEDs, organic solar cells and fluorescent probes, due to their outstanding advantages like rigid structure, synthesis flexibility, good hole-transporting ability, photoconductivity, luminescence property, good thermal and photochemical stability [24-27]. D-A configured carbazole based dyes used as active photosensitizers are also reported in the literature [28]. Among them, CBP (4,4'-N,N'-dicarbazole-biphenyl) and mCP (1,3-di(9Hcarbazol-9-yl)benzene) are the most commonly used carbazole-based hosts. Unfortunately, the two compounds exhibit poor thermal stability with low glass transition temperatures (CBP: 62 °C, mCP: 60 °C) [29]. On the other hand, symmetrical and unsymmetrical substituted oxadiazole (OXD) derivatives more particularly 2,5-diaryl-1,3,4-oxadiazoles are extensively used as multipurpose electron-transporting/hole-blocking materials in OLEDs/optoelectronic devices, due to their good electron-transporting/hole-blocking nature and high thermal stability, thereby increasing the quantum yield of fluorescence  $(\Phi_f)$  [18, 23, 30].

Against this background, in the present work we have designed, synthesized and characterized a new D- $\pi$ -A configured heterocyclic bipolar fluorophore carbazole-oxadiazole (CBZ-OXA-IV) based organic dye. Photophysical properties of the compound CBZ-OXA-IV have been thoroughly examined by using UV-visible and fluorescence emission spectra. Optical band gaps  $(E_g^{opt})$  and fluorescence quantum yields  $(\Phi_f)$ were calculated. Intramolecular charge transfer (ICT) properties of the synthesized bipolar fluorophore CBZ-**OXA-IV** have been investigated with the help of solvent polarity effects (solvatochromism) in various solvents with variations in solvent polarity from polar to non polar solvents. Further, with the aim of understanding their molecular geometry and electronic distribution in their frontier molecular orbitals, the Density Functional Theory (DFT) computations including MESP maps and natural bond orbital analysis were performed using the Gaussian 09 software and the ground state geometries were optimized at CAM-B3LYP and 6-311G (d,p) level of study. Additionally, the electrochemical properties of the bipolar fluorophore CBZ-OXA-IV was carried out by using the cyclic voltammetry (CV) measurements. From the DSC and TGA measurements, the thermal stability of the fluorophore was confirmed. The current results indicates that the synthesized Donor- $\pi$ -Acceptor configured bipolar fluorophore carbazole-oxadiazole (CBZ-OXA-IV) based organic dye is a promising candidate and could play an important role in the field of OLEDs/optoelectronic devices.

#### **Results and Discussion**

#### **Design and Synthesis**

As shown in Scheme 1, a relatively simple and efficient synthetic pathway is utilised for the synthesis of the designed bipolar target compound **CBZ-OXA-IV**. The primary key intermediates were prepared according to the our previously



published and literature procedures [31, 32]. In short, synthesis of the intermediate compounds and target fluorophore were described as follows, 4-methylbenzohydrazide and 4-(tert-butyl)benzoic acid were taken in POCl<sub>3</sub> and refluxed for 12 h at 100 °C to get the intermediate compound 2-(4-(tert-butyl)phenyl)-5-(p-tolyl)-1,3,4-oxadiazole (I). Subsequently NBS bromination is carried out at the allylic position of the compound I by using N-Bromosuccinimide in the presence of catalytic amount of dibenzoyl peroxide (DBP) in CCl<sub>4</sub> heating at 80 °C for 8 h gave the required intermediate compound 2-(4-(bromomethyl)phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (II). Further, the nucleophilic substitution reaction of triphenyl phosphine at the allylic brominated carbon of compound II was carried out by taking, a mixture of triphenyl phosphine and compound II in ethyl acetate, refluxing for 8 h at 80 °C gives Wittig salt (III). The intermediate compound 4-(9H-carbazol-9-yl) benzaldehyde was prepared according to published procedure [33]. A solution of 4-fluorobenzaldehyde, carbazole and K<sub>2</sub>CO<sub>3</sub> were taken in DMSO was heated at 150 °C overnight to yield the intermediate compound 4-(9H-carbazol-9-yl)benzaldehyde. In the final step, a mixture of phosphonium salt (III) and 4-(9H-carbazol-9-yl)benzaldehyde were taken in a round bottom flask containing DCM:water (60:40) mixture. To the reaction mixture 50% NaOH was added dropwise and reaction was stirred for 10 h at room temperature with continuous vigorous stirring leads to the formation of required bipolar fluorophore CBZ-OXA-IV via Wittig reaction. The product was readily purified on silicagel column chromatography by using ethyl acetate/hexane as eluent to get light green coloured solid in good yield. The synthesized compound CBZ-OXA-IV is stable in an ambient atmosphere containing oxygen and moisture. The fluorophore CBZ-OXA-IV is fully characterized by using various spectroscopic techniques like <sup>1</sup>H, <sup>13</sup>C NMR, FT-IR and LC-MS/ESI-MS. The data obtained were well consistent with the proposed chemical structure of the bipolar compound of CBZ-OXA-IV.

#### **Photophysical Properties**

#### UV–Visible Absorption and Photoluminescence Properties

Optical spectroscopy is a powerful tool to study the interaction of light and matter [34]. For the better understanding of nature of electronic transitions and to get deeper inside the optical properties of organic bipolar fluorophore **CBZ-OXA-IV** for the feasible applications in optoelectronic devices/OLEDs, the UV–vis absorption and photoluminescence spectra were measured in ethanol (EtOH) solution are shown in Fig. 1(A and B), respectively. The corresponding optical data ( $\lambda_{max}^{abs}$ ,  $\lambda_{max}^{emi}$  and Stokes shift) are summarized in Table 1. In the absorption spectrum of **CBZ-OXA-IV** dye (Fig. 1A), displayed two distinct absorption bands centred at one in higher wavelength region (strong band) 353 nm and in the lower wavelength region (weak band) 292 nm. The relatively weak band observed at 292 nm can be ascribed to the localized  $\pi$ - $\pi$ \* transition of the electron rich carbazole donor species of the dye. While, the intense band observed at 353 nm is attributed to delocalized  $\pi$ - $\pi$ \* electronic transition or ICT (intermolecular charge transfer) from the donor to acceptor unit (carbazole to oxadiazole group through extended  $\pi$ -conjugation) [31, 35].

Photoluminescence spectrum of fluorophore CBZ-OXA-IV displayed a single emission peak at 470 nm in ethanol solution at room temperature have been shown in Fig. 1(B)and the resultant emission maxima  $(\lambda_{max}^{emi})$  is summarized in Table 1. The bipolar fluorophore CBZ-OXA-IV have deep blue emission. As compared to the absorption spectrum the emission maxima was red shifted. Furthermore, the Stokes shift was calculated from the difference between  $\lambda_{max}^{abs}$  and  $\lambda_{max}^{emi}$  values and it was found to be 7052 cm<sup>-1</sup>. Usually a small Stokes shift can cause self-quenching of fluorescence and measurement error by excitation light and scattered light [36]. Fascinatingly, the CBZ-OXA-IV dve shown high Stokes shift about 7052  $\text{cm}^{-1}$ . The main advantage of the high Stokes shift organic fluorophores is the minimization of the reabsorption of fluorescence photons by the dye. High fluorescence Stokes shift is critical for expands the field of their practical application, for example, solid state fluorophores including those applied in OLEDs, fluorescence imaging measurements, fluorescent sensing compounds, several biophysical and analytical applications, etc. [37]. The new CBZ-OXA-IV dye has some important features, such as a large Stokes shift (7052  $\text{cm}^{-1}$ ) and significantly stronger deep blue fluorescence. Here, the higher stokes shift value of CBZ-OXA-IV can be accounted to an excited-state intramolecular charge transfer (ICT) between the electron donor carbazole group to electron acceptor 1,3,4-oxadiazole group through  $\pi$ -extended conjugation in the dye.

The extensive applicability of organic materials that show strong fluorescence in the solid-state have broad applications, such as OLEDs, OFETs, organic lasers and solid-state fluorescence sensors [38, 39]. On the other hand, organic materials that exhibit fluorescence in dilute solutions generally suffer from quenched or reduced fluorescence intensity in their solid-state because of aggregation-caused quenching (ACQ) [38]. In order to achieve strong fluorescence in solid-state form of dye requires the prevention of intermolecular interactions between neighboring fluorophores, which causes fluorescence quenching [38]. In the light of this factor, introduction of bulky substituent groups into a backbone of fluorophore is an effective strategy to enhance the solid-state fluorescence by preventing intermolecular interactions, such as  $\pi$ - $\pi$  interactions [38]. Utilizing this approach, we have reported solid-state fluorescent dye



Fig. 1 (A) UV-vis absorption spectrum and (B) Photoluminescence spectrum of the fluorophore CBZ-OXA-IV in ethanol solution at r.t (C) Normalized fluorescence spectrum of CBZ-OXA-IV in solid state (thin film). Ref—Coumarin 480 dye is used for comparison

**CBZ-OXA-IV** containing bulky carbazole as donor group which is twisted by about 56.96° from the plane of the rest of the dye (see in Table 3). Emission spectrum of bipolar fluorophore **CBZ-OXA-IV** recorded in solid state form (thin films) is shown in Fig. 1(C) and resultant emission maxima  $(\lambda_{max}^{emi})$  is observed at 470 nm (violet to red color) (Table 1). It is quite interesting to notice, that there is no shift in the emission maxima form the solution to solid state emission maxima. This is presumably due to lesser intermolecular interactions that take place between neighboring molecules in the solid state.

**Table 1** Summary of photophysical properties, optical bandgap energies  $(E_g^{opt})$ , fluorescence quantum yields  $(\Phi_f)$  and thermal properties of bipolar fluorophore **CBZ-OXA-IV** 

Compound	$\lambda_{max}^{abs}$ (nm) <sup>[a]</sup>	$\lambda_{max}^{emi}$ $(nm)^{[b]}$	$\lambda_{max}^{emi}$ $(nm)^{[c]}$	Stokes shift (cm <sup>-1</sup> )	$E_g^{opt[\mathbf{d}]}$ (eV)	Quantum Yield ( $\Phi_f$ )	$T_{\rm g}  [^{\rm o}{\rm C}]^{\rm [e]}$	$T_{\rm m}  [^{\rm o}{\rm C}]^{[\rm e]}$	$T_{\rm c}  [^{\rm o}{\rm C}]^{\rm [e]}$	T <sub>5d</sub> [°C] <sup>[e]</sup>
CBZ-OXA-IV	353	470	470	7052	3.01	0.40	98	207	-	387
Ref. C480	354	428	-	4884	-	0.98	-	-	-	-

<sup>[a]</sup>Absorption maxima ( $\lambda_{max}^{abs}$ ) in ethanol at 10 µM concentration.

<sup>[b]</sup>Emission maxima ( $\lambda_{max}^{emi}$ ) in ethanol at 10 µM concentration.

<sup>[c]</sup>Emission maxima measured in solid state (thin film).

<sup>[d]</sup>Optical band gap energies  $(E_g^{opt})$  were calculated from the long edge of the absorption spectrum using  $E_g^{opt} = hc/\lambda = 1240/\lambda$  (eV).

<sup>[e]</sup>Results from DSC and TGA measurements;  $T_g$ -glass transition temperature,  $T_m$ -melting temperature,  $T_c$ -crystallization temperature and  $T_{5d}$ -5% weight loss temperature. Ref-Coumarin 480.

# Optical Band Gap $(E_g^{opt})$

The determination of the optical band gap  $(E_g^{opt})$  is a necessary parameter to be considered for the application of organic probes in the field of photovoltaics and organic lightemitting devices/optoelectronic devices, as the  $E_{g}^{opt}$  provide basics in the understanding of the optical as well as the electrical process occurring within the organic materials [40]. The value of  $E_a^{opt}$  describes the fundamental light absorption edge, which gives the information about the amount of light energy required to promote electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [41]. As the optical bandgap  $(E_g^{opt})$  of organic molecules mainly depends on the bond length alternation pattern, planarity, aromaticity and electron-withdrawing/releasing substitutions [42]. Therefore tuning the optical band gap into the desired value for applications is of utmost importance. Optical band gap  $(E_g^{opt})$  of the bipolar fluorophore CBZ-OXA-IV is estimated from the absorption edge (long wavelength edge) of the corresponding absorption spectra ( $\lambda_{onset}$ , solution) to the baseline make use of the Eq. (1) [43] and the corresponding value is tabulated in Table 1.

$$E_g^{opt} = \frac{1240}{\lambda onset} \tag{1}$$

The optical band gap  $(E_g^{opt})$  value of the bipolar fluorophore **CBZ-OXA-IV** is found to be 3.01 eV. The low optical band gap  $(E_g^{opt})$  value of the fluorophore **CBZ-OXA-IV** reveals the increase in the extended  $\pi$ -conjugation from the electron donor carbazole to electron acceptor 1,3,4-oxadiazole group. Due to that reason, it is encouraging to use of fluorophore **CBZ-OXA-IV** for the possible application in the optoelectronic devices.

#### Solvatochromism Studies

Solvatochromism is a simple yet robust phenomenon through which we can study few important properties of the solute. The interaction between solute and solvents largely reflect the real nature of the solute molecule. Solvatochromism can shed light on the effects of molecular environment on the photophysical behavior of the solute. Solvents with different polarities show different peak intensities, which can be accounted to H-bonding, intramolecular charge transfer (ICT) and many other complex phenomena that occurs between molecules [44]. In addition, the change in a solvent is complemented by a change in polarity, dielectric constant and polarizability of the medium. Therefore, the ground and excited state of the organic materials are affected by changing solvent [45]. In order to investigate the solvent polarity effects (solvatochromism) on bipolar fluorophore CBZ-OXA-IV have been carried out in various solvents such as, polar/less polar protic solvents methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, nonanol, decanol and in polar aprotic solvents like DMSO, acetonitrile and DMF. Additionally, weakly/non-polar solvents namely chloroform, toluene, 1,4-dioxane, octane, decane, tetradecane and hexadecane were also studied. The normalized absorption spectra and fluorescence emission spectra of the compound CBZ-OXA-IV in various solvents with varying polarities are shown in Fig. 2(A, B and C). Corresponding photophysical data (absorption maxima, emission maxima and Stokes shift) have been enlisted in Table 2. The compound CBZ-OXA-IV exhibited a hypsochromic shift (blue-shift) of about 17 nm as the polarity of the solvents (in case of polar/less polar protic) increased gradually from decanol to methanol. This clearly suggests that higher the polarity of the solvents, higher is the energy of excitation. This is very similar to the nature we have observed in our work on pyrene substituted 1,3,4-Oxadiazole derivatives, whose results reveal, irrespective of functionalization, the solvent effects remain same for 1,3,4-oxadiazole based dyes [31]. The ground state is highly stable in alcohols, which can be verified looking into the small shifts in peaks (maximum 9 nm shift between methanol and ethanol; in all other solvents, the shift is 1-3 nm). We can observe very similar trends in case of weakly polar solvents. For solvents with more polar nature the excitation energy is high. And as we move towards more weakly polar solvents, we can observe the shifts towards red region. Contrarily, in case of highly polar solvents, we observe a hypsochromic shift, to which the intermolecular dipole interaction may be made responsible.

In case of fluorescence, we have observed positive solvatochromism (red shifted emission) in polar protic solvents (polarity of the solvents increased gradually from decanol to methanol) and polar aprotic solvents (polarity of the solvents increased gradually from DMF to DMSO) are mainly due to the fact that the excited state of the compound CBZ-OXA-IV is influenced by the dipole-dipole interaction and solute-solvent interaction. This indicates a larger change in dipole moment and stronger intramolecular charge transfer character of bipolar fluorophore CBZ-OXA-IV between the carbazole donor unit to the electron acceptor oxadiazole moiety through  $\pi$ -conjugation. Also, it is evident by the large Stokes shifts of the fluorophore CBZ-OXA-IV found to be in the range 3887- 8365  $\text{cm}^{-1}$  (Table 2). Furthermore, intramolecular charge transfer (ICT) character of bipolar fluorophore CBZ-OXA-IV is confirmed by using theoretical density functional theory (DFT) computations. However, we observed bathochromic/hypsochromic shifts in the emission properties of the molecule solvated in weakly/ non polar solvents. A major distinction is dual fluorescence



Fig.2 (A) Normalized absorption and emission spectra of organic fluorophore CBZ-OXA-IV in polar/less polar protic solvents. (B) Normalized absorption and emission spectra of organic fluorophore

**CBZ-OXA-IV** in polar aprotic solvents. (C) Normalized absorption and emission spectra of organic fluorophore **CBZ-OXA-IV** in weakly/non polar solvents

Table 2	Solvatochromism:	Absorption	and	emission	parameters	of
organic	fluorophore CBZ-C	<b>XA-IV</b> in d	iffere	nt solvents	s	

Solvent	CBZ-OXA	-VI	
	$\overline{\lambda_a}$	$\lambda_{f}$	Stokes shift
Polar protic solvents			
Methanol	346	485	8283
Ethanol	353	470	7052
Propanol	356	466	6630
Butanol	358	463	6334
Pentanol	358	461	6240
Hexanol	359	457	5973
Octanol	361	451	5527
Nonanol	363	447	5176
Decanol	363	446	5126
Polar aprotic solvents			
DMSO	359	487	7321
Acetonitrile	351	476	7481
DMF	354	473	7106
Weakly/Nonpolar solvents			
Chloroform	356	415/495	7887
Toluene	361	418/435	4712
1,4-dioxane	344	413/483	8365
Octane	360	399/422	4081
Decane	362	389/465	6118
Tetradecane	364	402/424	3887
Hexadecane	364	393/465	5967

 $\lambda_a$  Absorption maxima in nm,  $\lambda_f$  Emission maxima in nm and Stokes shift in  $\text{cm}^{-1}$ 

peaks (Fig. 2(C)), which signify various intramolecular processes such as protonated species, excimers, dimers, excited state photoisomers and TICT [46]. Additionally, we can also observe a fluctuation in shifts, which are irrespective of polarity values. This may be attributed to various solvent–solute interactions. In case of highly polar aprotic solvents, a bathochromic shift has been returned by the system. Overall, the performance of this novel molecule is useful in case of highly polar solvents (shown positive solvatochromism). This suggests that the molecule is a good optical material with a highly stabilized structure and molecular orbitals. But the variations observed in emission properties of the molecule in weakly/non polar solvents needs a higher level of micro environmental study, which may be the scope of our future work.

# **Theoretical Computations**

The investigation of frontier molecular orbitals (FMOs) is recognized to be significant since they are directly connected to the photophysical properties of the organic materials, such as hole/electron injection, absorption and emission. Further, the energy levels of the FMOs of the organic compounds are dependent on the distribution of the frontier molecular orbitals. In addition, the optical behavior and electronic properties of the organic materials rely mainly on the changes in the ground state electronic structure  $(S_0)$ , making it imperative to inspect the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) and band gaps (HOMO-LUMO gap) of the organic fluorophore in the ground state  $(S_0)$  [47, 48]. In order to understand the electronic states, molecular geometries and intramolecular charge transfer (ICT) properties of the synthesized bipolar fluorophore CBZ-OXA-IV, Density Functional Theory (DFT) calculations were performed by using the Gaussian 09 software [49]. The ground state ( $S_0$ ) geometries of CBZ-OXA-IV dye were optimized using CAM-B3LYP/6-311G (d,p) level of theory.

#### **Frontier Molecular Orbitals (FMO)**

Frontier molecular orbitals (FMO) amplitude plots of highest occupied molecular orbitals and lowest unoccupied molecular orbitals of fluorophore CBZ-OXA-IV show in Fig. 3 and corresponding data are summarized in Table 3. As shown in Fig. 3 the electron density of highest occupied molecular orbitals (HOMO) are mainly located on the electron-donating carbazole moietie. On the other hand, the lowest occupied molecular orbitals (LUMO) on the electron-deficient 1,3,4-oxadiazole ring. This clearly indicates that the presences of intramolecular charge transfer (ICT) properties of the fluorophore CBZ-OXA-IV from electron-donating carbazole group (D) to electron accepting 1,3,4-oxadiazole group (A) through phenyl  $\pi$ -linker, thereby reducing to the D- $\pi$ -A form. Almost complete separation of HOMO/LUMO energy levels (Fig. 3) suggests that the separation of electron cloud of HOMO/LUMO could afford the transporting channels between hole and electrons, which may endow the fluorophore CBZ-OXA-IV with the ability of bipolar charge transport. The separation of the HOMO and LUMO is efficient for charge carrier transfer and balance in the emitter layers of OLEDs [50]. The theoretical HOMO and LUMO energy levels of CBZ-OXA-IV were found to be -5.82 and -1.76 eV, respectively. The theoretical band gap  $(E_{o})$  determined from the difference between the HOMO and LUMO energy value from DFT calculations is found to be 4.06 eV (Table 3).

From Table4, by using the ground state optimized molecular structure of compound **CBZ-OXA-IV**, the dihedral angles (DA) [°] are calculated around the different groups are found to be i/ii 56.96, ii/iii 0.04 and iii/iv 0.17. The large dihedral angle observed between the carbazole group and adjacent phenyl ring about 56.96 ° indicates the twisted nature of the carbazole plane from the rest of

**Fig. 3** Density functional theory (DFT) computations: HOMOs and LUMOs levels of bipolar fluorophore **CBZ-OXA-IV** at the CAM-B3LYP/6-311G (d,p) level of theory in the gas phase



#### LUMO

1,3,4-oxadiazole core. Large DA angles are beneficial for suppressing quenching of their fluorescent caused by the aggregation of molecules in the solid states [50].

#### Molecular Electrostatic Potential Surface (MESP) Analysis

The molecular electrostatic potential (MESP) analysis is an important tool to predict the molecular properties and reactivity of the organic dyes. MEP surface plot helps to exemplify chemical phenomenon such as reactivity, bonding, resonance, inductive effect and hydrogen bonding interactions. The calculated electrostatic potential surface (ESP) plot of **CBZ-OXA-IV** dye shown in Fig. 4, computed using their ground state optimized geometry on the corresponding molecular surface. In addition, the obtained ESP maps demonstrate the three dimensional charge distributions in the fluorophore. In general, the areas of electrostatic potential in terms of color increase from blue <sup>5</sup> green <sup>5</sup> yellow <sup>5</sup> orange <sup>5</sup> red [28]. The most electronegative potential (red color) are mainly localized above the electron accepting 1, 3, 4-oxadiazole unit, thus indicating the abundance of electrons in the red region of fluorophore. While, the most

Table 3 Calculated frontier molecular energy levels and electrochemical properties of bipolar fluorophore CBZ-OXA-IV

Compound	HOMO <sup>[a]</sup> (eV)	LUMO <sup>[a]</sup> (eV)	E <sub>ox</sub> <sup>onset [b]</sup> (eV)	HOMO <sup>[C]</sup> (eV)	LUMO <sup>[d]</sup> (eV)	$E_g^{opt[e]}$ (eV)	$\frac{E_g^{[f]}}{(eV)}$
CBZ-OXA-IV	-5.82	-1.76	1.28	-5.72	-2.71	3.01	4.06

<sup>[a]</sup>The HOMO and LUMO values from DFT calculations.

<sup>[b]</sup>The onset oxidation potential.

<sup>[c]</sup>Calculated HOMO from the onset oxidation potential of the compound  $E_{HOMO} = -[E_{ox}^{onset} + 4.44]$ (eV).

<sup>[d]</sup>Estimated LUMO using empirical equation  $E_{LUMO} = -[HOMO + E_g^{opt}](eV).$ 

<sup>[e]</sup>Optical band gap energies were calculated from the equation  $E_g^{opt} = hc/\lambda = 1240/\lambda$  (eV), where  $\lambda$  is the edge wavelength (in nm) of the UV–Vis absorption spectrum.

<sup>[f]</sup>The theoretical band gap  $(E_v)$  determined from the difference between the HOMO and LUMO energy values from DFT calculations.



Table 4 Dihedral angles (DA) [°] are calculated around carbazole group, phenyl and 1,3,4-oxadiazole group from ground state optimized molecular structure of CBZ-OXA-IV

positive electrostatic potential (blue color) localized above the electron donating carbazole group and phenyl rings. This gives the additional confirmation for the presence of strong intramolecular charge transfer properties from donor (D) to acceptor (A) group of the  $\pi$ -conjugated **CBZ-OXA-IV** dye.

#### **Comparison of IR Spectra**

We have obtained optimized structure of CBZ-OXA-IV, combined with frequency calculations to attain more stabilized global minima. Here we consider studying the FT-IR spectra which is indeed absorption spectrum due to various significant vibrations in the molecule. In order to get more precise results, comparison of simulated and experimental outcomes can be considered. We have presented a combination of graphs put together in Fig. 5, so that the similarities can be easily identified. Both the plots have transmittance peaks at relatively similar distances with an overall shift due to differences in the surroundings. The important peaks which actually characterize the molecule are given in Table 5 with comparison between experimental data and simulated data obtained using DFT/CAM-B3LYP theory with 6-311G (d,p) basis set. The compared data reveal that there is a shift in DFT simulated data of around 50 cm<sup>-1</sup>

with reference to the experimentally obtained data. However, the position and relative intensities of the peak justify that both of these results can be compared and put together to confirm the structural and vibrational properties of the molecule. The simulated data leads the experimental values, whose difference goes on decreasing as we move towards to lower wavenumber region. The absorption due to C–O–C asymmetric oscillation in oxadiazole ring has the minimum shift. Since the oxadiazole ring is the dominant piece of structure in the molecule, environmental effects and other perturbations during experiment may have reduced, leading to the minimum shift in the wavenumbers.

#### **Natural Bond Orbital (NBO) Analysis**

Natural bond orbital analysis stands one of the best methods to understand the molecular orbitals very similar to the classical Lewis orbital structure [51]. It is a multi-step calculation process, in which the initial calculations consider each atom as unbound and their atomic orbitals are taken. Such simple atomic orbitals are then combined with the molecular bonding and antibonding orbitals [51]. This effectively gives the terminal step of determining the natural bond orbitals of the molecule thus formed [51]. We did NBO calculations **Fig. 4** Ground state (S<sub>0</sub>) optimized geometry and MEP surface plot for compound **CBZ-OXA-IV** at CAM-B3LYP and 6-311G (d,p) level of theory



Ground state optimized structure





**Molecular Electrostatic Potential (MEP)** 





5.556e-2

Table 5 Comparison of IR peaks of simulated and experimental data for CBZ-OXA-IV with assignment of their groups

	-	
FT-IR Peaks (cm <sup>-1</sup> )		Assignment
Experimental	Simulated	
3052	3090	C-H Aromatic
2955	3022	C-H Aliphatic
1600	1654	C–C Olefinic
1547	1590	C=C Aromatic
1514	1542	C=N Aromatic
1227	1230	C–O–C Asymmetric Oxadiazole ring
1067	1078	C–O–C Symmetric Oxadiazole ring

using DFT/CAM-B3LYP/6-311G (d,p) level in Gaussian 09 package to get this information. It also gives useful information on intramolecular bonding and the interactions between them, which can also be further extended to understand the charge transfer process in the molecule [52].

The results of NBO can also be used to get the information about interactions of filled and virtual orbitals, which help in analysis of intra and intermolecular interactions. Inorder to get the donor–acceptor interactions through NBO, we have employed second order Fock matrix as the base as we have seen the same in few literature [53, 54]. By second order perturbation theory, for every acceptor (j) and donor (i), the stabilization energy (E (2)) associated with  $i \rightarrow j$ delocalization can be estimated to be,

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(E_j - E_i)}$$
(2)

Here,  $(F_{ij})^2$  is the fock matrix element which is off-diagonal between i and j,  $q_i$  is the donor orbital occupancy and  $E_i$ ,  $E_i$  are the energies of diagonal elements.

In this particular case, we have considered the donor acceptor pairs with distinctively high stabilization energy (E (2)) only. The lists of all such important pairs are enlisted in Table 6. Some notable donor-acceptor pairs are  $\pi^*(C54-C58) \rightarrow \pi^*(C64-C68)$  with an energy (E (2)) value of 344.00 kcal/mol and  $\pi^{*}(C53-N56) \rightarrow \pi^{*}(C61-C65)$ with an energy of 344.76 kcal/mol. Some of the other important donor  $\rightarrow$  acceptor interactions are  $\sigma$  (Lone pair N73)  $\rightarrow \pi^*(C54-C58)$  and  $\pi^*(C53-C56)$ ,  $\pi$  (Lone pair O18)  $\rightarrow \pi^*(C15-N16)$  and  $\pi^*(N17-C19)$  with energies with 42.68 and 42.70, 43.41 and 43.33 kcal/ mol respectively. The electron occupancy ratios and the percentage of p and s-character in the above NBOs have been collected in Table 7. We have observed almost 100% p-character in the natural atomic orbitals of donors with E(2) higher than 35 kcal/mol. The labels and symbols can be associated with the optimized structure shown before in Fig. 4.

#### **Electrochemical Properties**

In order to choose new organic materials for optoelectronic devices/OLEDs applications, it is very important to know the energy levels of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the band gap between them. In this regard, the most useful method to characterize the organic materials and estimate the energy band gap is cyclic voltammetry. For organic materials, HOMO represents the energy required to remove an electron from a molecule, which is an oxidation process and LUMO is the energy required to inject an electron to a molecule, thus implying a reduction process [55]. Thus, the electrochemical property of bipolar fluorophore CBZ-OXA-IV was probed by cyclic voltammetry (CV). The cyclic voltammogram of CBZ-OXA-IV is presented in Fig. 6 and the corresponding electrochemical data are summarized in Table 3. CV was carried out in a three-electrode cell with a Pt counter electrode, an Ag/AgCl reference electrode and a glassy carbon working electrode at a scan rate of 100  $mVs^{-1}$  with 0.1 M  $nBu_4NPF_6$  as the supporting electrolyte, in anhydrous acetonitrile solution at room temperature under N2 atmosphere. Fluorophore CBZ-OXA-IV showed oxidation onset potential at 1.28 eV. The compound exhibits both reversible oxidation and reduction behaviour, which suggests its potential for efficient hole/electron transport. On the basis of the obtained oxidation onset potential, the HOMO and LUMO energy levels of fluorophore CBZ-OXA-IV is calculated by using the Eqs. (2) and (3) [56].

$$\mathbf{E}_{HOMO} = -\left[E_{ox}^{onset} + 4.44\right](eV) \tag{3}$$

$$\mathbf{E}_{LUMO} = -\left[HOMO + E_g^{opt}\right](eV) \tag{4}$$

The HOMO energy level of **CBZ-OXA-IV** dye determined from the onsets of the oxidation potential is found to be -5.72 eV and the LUMO energy level of **CBZ-OXA-IV** dye is estimated using empirical equation  $E_{LUMO} = -[HOMO + E_g^{opt}]$  (eV) is

Table 6 Analysi	is of second order po	erturbation theory of F	ock matrix in NBO b	asis with respect to the	he intra-molecular bon	ds of the compound (	BZ-OXA-IV		
Donor	Type	ED/e	Acceptor	Type	ED/e	$\mathrm{E}(2)^{\mathrm{a}}$	E(j)-E(i) <sup>b</sup>	F(i,j) <sup>c</sup>	
C54-C58	я* В	0.45585	C64-C68	π*	0.31618	344.00	0.01	0.097	
C53-C56	μ*	0.45586	C61-C65	μ*	0.31628	344.76	0.01	0.097	
C20-C25	я* К	0.37666	C23-C24	μ*	0.32227	307.93	0.01	0.098	
			C21-C22	π*	0.28496	299.91	0.01	0.096	
N17-C19	μ*	0.27824	C20-C25	μ*	0.37666	181.19	0.01	0.080	
C15-N16	ж*	0.28025	C11-C12	π*	0.38090	228.53	0.01	0.083	
C9-C10	я* Я	0.38182	C7-C8	μ*	0.11022	47.17	0.03	0.071	
C4-C5	μ*	0.36970	C7-C8	μ*	0.11022	45.95	0.03	0.071	
LP N73	ъ	1.66034	C54-C58	μ*	0.45585	42.68	0.37	0.116	
			C53-C56	μ*	0.45586	42.70	0.37	0.116	
LP 018	н	1.71952	C15-C16	μ*	0.28025	43.41	0.46	0.127	
			N17-C19	μ*	0.27824	43.33	0.47	0.127	
C23-C24	н	1.64854	C20-C25	π*	0.37666	34.52	0.36	0.100	
C7-H48	ð	1.97585	C8-H47	a*	0.01704	5.61	1.08	0.070	
N16-N17	ð	1.97143	C19-C20	ە*	0.03447	6.35	1.40	0.084	
<sup>a</sup> E(2) is the ener	gv difference of hyr	per-conjugative interact	ions (stabilization en	ergv in kJ/mol)					
<sup>b</sup> Energy differen	ice (a.u.) between de	onor and acceptor i and	l j NBO orbitals						
°F(i,j) is the Foc	k matrix elements (	a.u.) between i and j N	BO orbitals						

Bond (A–B)	ED/energy (a.u.)	EDA%	EDB%	NBO	s %	р %
π* C54-C58	0.45585	52.19	47.81	0.7224(sp <sup>1.00</sup> )C54	0.00	99.96
				-0.6915(sp1.00)C58	0.00	99.96
π* C53-C56	0.45586	52.19	47.81	0.7224(sp1.00)C53	0.00	99.96
				-0.6915(sp1.00)C56	0.00	99.96
π* C20-C25	0.37666	46.78	53.22	0.6840(sp <sup>1.00</sup> )C20	0.00	99.98
				-0.7295(sp1.00)C25	0.00	99.95
π* N17-C19	0.27824	41.73	58.27	0.6460(sp <sup>1.00</sup> ) N17	0.00	99.79
				-0.7634(sp <sup>1.00</sup> )C19	0.00	99.78
π* C15-N16	0.28025	58.00	42.00	0.7616(sp <sup>1.00</sup> )C15	0.00	99.80
				-0.6481(sp1.00)N16	0.00	99.96
π* C9-C10	0.38182	50.22	49.78	0.7087(sp <sup>1.00</sup> )C9	0.00	99.95
				-0.7055(sp1.00) C10	0.00	99.96
π* C4-C5	0.36970	49.27	50.73	0.7019(sp <sup>1.00</sup> )C4	0.00	99.96
				-0.7122(sp <sup>1.00</sup> ) C5	0.00	99.95
σ LP N73	1.66034	-	-	sp <sup>1.00</sup>	0.00	100.0
π LP 018	1.71952	-	-	sp <sup>1.00</sup>	0.00	99.93
π C23-C24	1.64854	48.37	51.86	0.6952(sp <sup>1.00</sup> ) C23	0.00	99.94
				-0.7189(sp <sup>1.00</sup> ) C24	0.00	99.95
σ C7-H48	1.97585	59.71	40.29	0.7727(sp <sup>2.79</sup> ) C7	26.36	73.55
				+0.6347(sp <sup>2.79</sup> ) H48	26.36	73.55
σ N16-N17	1.97143	50.04	49.96	0.7074(sp <sup>3.08</sup> ) N16	24.50	75.34
				+0.7068(sp <sup>3.08</sup> ) N17	24.44	75.39

Table 7NBO results exhibitingthe formation of Lewis and non-Lewis orbital for CBZ-OXA-IVwith S and P orbital formationpercentage

found to be -2.71 eV, indicating that deep HOMO/LUMO energy levels possess good electron-transporting and the good hole transporting properties. In addition, HOMO/LUMO energy levels of **CBZ-OXA-IV** dye calculated from the DFT computations were found to be -5.82 and -1.76 eV, respectively (Table 3), which are in good agreement with the HOMO/ LUMO energy level values measured using CV. Also, it is interesting to notice that the theoretical band gap ( $E_g$ ) determined from the difference between the HOMO and LUMO energy



Fig. 6 Cyclic voltammogram of bipolar fluorophore CBZ-OXA-IV

values from DFT calculations is found to be 4.06 eV and is in good agreement with the optical energy bandgap  $(E_g^{opt})$  estimated from the absorption edge of UV–Vis spectra 3.01 eV. These results revealed the facile reversible redox behaviour of the synthesized bipolar fluorophore **CBZ-OXA-IV** and the energy band gap was determined by both experimentally and theoretically which is found to be an average of 3.53 eV, suggesting that they can be applied as bipolar transport materials for electroluminescence applications in optoelectronic devices/ OLEDs.

#### **Thermal Properties**

In order to use the organic materials for OLED/optoelectronic device applications, the thermal stability of organic materials is crucial factor in order to achieve high device stability and lifetime. For example, thermal instability or low glass transition temperatures Tg of an amorphous organic layer may result in the faster degradation of organic devices due to morphological changes and eventually device failure, fostered by the high temperatures that can occur during device operation [57, 58]. In order to address such challenges, it is required to synthesise novel organic materials having high thermal stability, glass transition temperatures (*Tg*) and 5% weight loss temperature (*T*<sub>5d</sub>) that ensure stable OLED/optoelectronic devices. The thermal stability of the new **CBZ-OXA-IV** dye was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry



Fig. 7 (A) DSC and (B) TGA curves of bipolar fluorophore CBZ-OXA-IV was carried out from 25–450  $^{\circ}$ C under N<sub>2</sub> atmosphere with a heating rate of 10  $^{\circ}$ C/min

(DSC) under N<sub>2</sub> atmosphere at scan rates of 10 °C/min in the temperature range from 25-450 °C, respectively. The obtained results were shown in Fig. 7(A and B) and the corresponding data were tabulated in Table 1. As shown in Fig. 7(A), the DSC curve reveal that endothermic peak is observed which correspond to melting point temperature  $(T_m)$  of the target fluorophore **CBZ-OXA-IV** found at 207 °C. The  $T_m$  of **CBZ-OXA-IV** was further confirmed by melting point instrument to be 210-211 °C. In addition, no exothermic peak corresponding to crystallization temperature  $(T_c)$  of the compound **CBZ-OXA-IV** was observed. In DSC curve, the synthesized compound reveal endothermic baseline shift due to the glass transition temperatures (Tg)for the compound CBZ-OXA-IV at 98 °C. It is quite interesting to notice that the glass transition temperatures (Tg) of CBZ-OXA-IV higher than popular and most often employed host materials in the literature, i.e., mCP (Tg = 60 °C), CBP (Tg = 62 °C), BCz1 (Tg = 67 °C), BCz3 (Tg = 77 °C) and TCz1 (Tg = 88 °C). Also, it is important to mention that the glass transition temperature (Tg) of **CBZ-OXA-IV** is higher than those of the most popular oxadiazole-based electron-transporting materials, such as, 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD, Tg = 60 °C), 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7, Tg = 77 °C) and is higher than the recently reported non-bipolar host-emitters that contain oxadiazoles (BOBP, Tg = 45 °C [59, 60]. The TGA curve reveal that the decomposition temperature ( $T_{5d}$  temperature, defined as the temperature at which organic compound loses its 5% weight) of bipolar fluorophore CBZ-OXA-IV under N<sub>2</sub> atmosphere was found at 387 °C. The high Tg and  $T_{5d}$  temperature of the CBZ-OXA-IV dyad may be due to a rigid and twisted structure of the carbazole branching unit attached to thermally

stable 1,3,4-oxadiazole group. These results suggest that synthesized bipolar molecule **CBZ-OXA-IV** provide desirable thermal properties, which are favourable for use in the OLED/organic electronic devices for fabrication of devices via vacuum sublimation without any decomposition and also as possible host materials in PHOLED.

#### **Experimental Section**

#### Fluorescence Quantum Yield ( $\Phi_f$ )

The quantum yield ( $\Phi$ ) is an important measure of luminescent/organic materials, which provides significant information about the excited state, coupling of electronic to vibrational states and radiationless transitions. Referring to the number of emitted photons per absorbed photons, it is an essential parameter that allows for primary classification of materials and detailed analyses of materials. However, it is also utilised to find out the appropriateness of laser material for media, sample purity and chemical structure [16, 61]. The fluorescence quantum yield ( $\Phi_f$ ) of the bipolar CBZ-OXA-IV dye is determined in ethanol solution by using a comparison method relative to a standard dye Coumarin 480 (2,3,5,6-1H, 4H-tetrahydro-8-methylquinolazino-[9, 9a,l-gh] coumarin) ( $\Phi$ ref=0.95) according to the Eq. (4) shown below [16]:

$$\Phi_f = \Phi_s \frac{F_u}{F_s} \frac{(OD_s)}{(OD_u)} \frac{\eta_u^2}{\eta_s^2}$$
(5)

where  $\Phi_s$  is the quantum yield of the standard reference,  $F_u$  and  $F_s$  are the integrated areas under the curve of emission spectra of unknown and standard sample,  $OD_u$  and  $OD_s$  is the optical density of the unknown and standard sample,  $\eta_u$  and  $\eta_s$  are the refractive index of both unknown and standard sample. The fluorescence quantum yield of **CBZ-OXA-IV** dyad is 0.40 in ethanol solution as depicted in Table 1. In the **CBZ-OXA-IV** dyad the presence of tert-butyl alkyl group results in better solubility as well as carbazole and 1,3,4-oxadiazole groups connected through phenyl and olefinic  $\pi$  spacer results in the extended  $\pi$ - $\pi$  conjugation. Due to the above reasons, it results in high fluorescence quantum yield of the bipolar compound and making it an excellent candidate for use in further applications like optoelectronic devices and OLEDs, so on.

#### **Materials and Synthesis**

All required starting materials and reagents were purchased from commercially available sources unless otherwise stated and used without further purification. Solvents used for synthesis and analytical/spectroscopic measurements were pre-dried and freshly distilled over appropriate drying reagents. The primary key intermediates ethyl 4-methylbenzoate, 4-methylbenzohydrazide and 2-(4-(tert-butyl)phenyl)-5-(p-tolyl)-1,3,4-oxadiazole were prepared according to the our previously published method [31, 32]. Carbazole, 4-methylbenzoic acid, 4-(tert-butyl)benzoic acid and 4-fluorobenzaldehyde were purchased from Sigma-Aldrich.

#### General Procedure for the Synthesis of Intermediates Ethyl 4-methylbenzoate and 4-methylbenzohydrazide:

To a suspension of 4-methylbenzoic acid (10.00 g, 73.50 mmol), dissolved in 80 mL of EtOH taken in a 250 mL RBF fitted with a dropping funnel and reflux condenser. Thionyl chloride (5.83 mL, 80.85 mmol) was added to the above reaction mixture slowly from the dropping funnel for 30 min at room temperature under constant stirring. The reaction mixture was refluxed for 8 h at 80 oC. The reaction mass was then cooled to room temperature and quenched with ice water under efficient fume hood. The resultant mixture was then extracted with ethyl acetate (3 X 30 mL), organic layer was washed with NaHCO<sub>3</sub> solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then organic layer was evaporated by rotary evaporation to afford intermediate compound ethyl 4-methylbenzoate in 95% yield.

A mixture of ethyl 4-methylbenzoate (8.00 g, 48.72 mmol) and hydrazine hydrate (2.60 mL, 53.59 mmol) in 60 mL

ethanol was charged into a single neck round-bottomed flask. The reaction mixture temperature was raised to reflux and continued for 10–12 h with stirring. After completion of the reaction as monitored by TLC, the reaction mass was allowed to cool to r.t. The reaction mixture was quenched with ice water and the precipitate obtained was filtered to give required intermediate 4-methylbenzohydrazide with 92% yield.

# General Procedure for the Synthesis of Intermediate 4-(9H-cacrbazol-9-yl)benzaldehyde:

The intermediate 4-(9*H*-carbazol-9-yl)benzaldehyde was synthesized according to the reported procedure [33]. A solution of 4-fluorobenzaldehyde (0.222 g, 1.79 mmol), carbazole (0. 30 g, 1.79 mmol), K<sub>2</sub>CO<sub>3</sub> (500 mg) and DMSO (10 mL) was heated at 150 °C overnight. After completion of the reaction as confirmed by thin layer chromatographic analysis (TLC), the solution was cooled to room temperature and water was added to the reaction mixture. The mixture was extracted thrice with DCM (3 X 10 mL) and the organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated a yellow solid was obtained, which is followed by recrystallization from EtOH yielding intermediate compound 4-(9H-carbazol-9-yl)benzaldehyde with 74% yield.

# General Procedure for the Synthesis of 2-(4-(tert-butyl) phenyl)-5-(p-tolyl)-1,3,4-oxadiazole (I):

Compound 4-methylbenzohydrazide (4.00 g, 26.63 mmol) and 4-(tert-butyl)benzoic acid (4.74 g, 26.63 mmol) were added to a 100 mL one-neck round bottom flask containing POCl<sub>3</sub> (20 mL). The mixture was refluxed for about 12 h at 100 °C with constant stirring. And then reaction mixture was cooled down to room temperature, the mixture was quenched with crushed ice under efficient fume hood. The obtained solid was filtered and washed with saturated sodium bicarbonate solution to remove unreacted carboxylic acid. The crude solid was recrystallized from EtOH to obtain the preferred intermediate compound 2-(4-(tert-butyl)phenyl)-5-(p-tolyl)-1,3,4-oxadiazole (I) in 86% as a white solid.

# 2-(4-(tert-butyl)phenyl)-5-(p-tolyl)-1,3,4-oxadiazole (I):

Colour: White solid. Obtained yield: 86%. MP=150–152 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.06 (d, *J*=8.5 Hz, 2H), 8.03 (d, *J*=8.2 Hz, 2H), 7.55 (d, *J*=8.5 Hz, 2H), 7.34 (d, *J*=8.4 Hz, 2H), 2.44 (s, 3H), 1.37 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.5, 155.0, 146.2, 138.4, 129.6, 127.4, 127.1, 125.6, 123.2, 123.1, 40.2, 31.5, 24.3; LC–MS: *m/z* calculated for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O 292.38200, found 292.36491 (M<sup>+</sup>).

# General Procedure for the Synthesis of 2-(4-(bromomethyl)phenyl)-5-(4-(tert-butyl) phenyl)-1,3,4-oxadiazole (II):

A mixture of 2-(4-(tert-butyl)phenyl)-5-(p-tolyl)-1,3,4oxadiazole (I) (3.0 g, 10.26 mmol) and catalytic amount of DBP (0.496 g, 0.2 equ) were added to CCl<sub>4</sub> (30 mL). To the above reaction mixture NBS (2.00 g, 11.28 mmol) was added and the reaction mixture was heated for 6–8 h at 80 °C. And then cooled and completion of the reaction was checked by TLC. The solvent was removed via rotary evaporation to get solid compound. Crude solid was washed repetitively with H<sub>2</sub>O to remove excess succinamide. The obtained crude solid was dried and recrystallized from ethanol to give pure 2-(4-(bromomethyl)phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4oxadiazole (II) in 87% yield as a white solid.

# 2-(4-(bromomethyl)phenyl)-5-(4-(tert-butyl) phenyl)-1,3,4-oxadiazole (II):

Colour: White solid. Obtained yield: 87%. MP=157–158 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.12 (d, *J*=8.2 Hz, 2H), 8.07 (d, *J*=8.5 Hz, 2H), 7.57–7.54 (d, 4H), 4.54 (s, 2H), 1.38 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.79, 163.88, 155.48, 141.34, 129.75, 127.31, 126.82, 126.10, 123.95, 120.98, 39.70, 35.13, 31.15; LC–MS: *m/z* calculated for C<sub>19</sub>H<sub>19</sub>BrN<sub>2</sub>O 371.27800, found 371.27610 (M<sup>+</sup>).

# General Procedure for the Synthesis of Wittig Salt (III):

2-(4-(bromomethyl)phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4oxadiazole (II) (2.0 g, 5.40 mmol) and PPh<sub>3</sub> (1.69 g, 6.48 mmol) were taken in ethyl acetate (20 mL) and stirred at r.t. The resulting mixture was refluxed for about 8 h at 80 °C. After the reaction, the obtained solid was filtered and washed with excess of EtOAc to remove un-reacted triphenyl phosphine to get the intermediate compound phosphonium salt (III) in 90% yield as white solid.

# Wittig Salt (III):

Colour: White solid. Obtained yield: 90%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.94 (d, *J*=8.5 Hz, 2H), 7.87 – 7.74 (m, 12H), 7.63 (m, 5H), 7.50 (d, *J*=8.5 Hz, 2H), 7.38 (dd, *J*=8.4, 2.6 Hz, 2H), 5.78 (d, *J*=15.3 Hz, 2H), 1.36 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.66, 163.69, 155.34, 134.98, 134.95, 134.61, 134.53, 132.57, 132.52, 131.65, 131.58, 130.17, 130.07, 126.75, 126.72, 126.68, 125.98, 123.55, 123.52, 120.72, 117.95, 117.26, 35.07, 31.11, 30.50, 30.13; LC–MS: *m/z* calculated for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>OP<sup>+</sup> 553.24033, found 553.25242 (M<sup>+</sup>).

# General Procedure for the Synthesis of (E)-2-(4-(4-(9H-carbazol-9-yl)styryl) phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (CBZ-OXA-IV):

A mixture of phosphonium salt (III) (0.30 g, 0.48 mmol) and 4-(9H-carbazol-9-yl)benzaldehyde (0.131 g, 0.48 mmol) were charged in a round bottom flask containing DCM:water (60:40) mixture. The reaction mixture was vigorously stirred and 50% NaOH (1 mL) was added dropwise to the mixture. The reaction was lasted for another 10 h at room temperature with continuous vigorous stirring. After the reaction completed, 20 mL DCM and 20 mL water respectively, were added to the reaction mixture. The organic layer was collected and washed with brine three times. The organic solvent was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and removed by rotary evaporator yielded a solid product. The crude product was purified by silica-gel column chromatography by using ethyl acetate/hexane as eluent to get target compound (E)-2-(4-(4-(9H-carbazol-9-yl)styryl)phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (CBZ-OXA-IV) in 83% yield as light green colour solid. The synthetic method is simple and highly efficient. The obtained target compound CBZ-OXA-IV is the trans configuration across the double bond is confirmed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR spectrum of the target compound CBZ-OXA-IV exhibit a doublet signals about 6.78 and 7.39  $\delta$  ppm with a typical coupling of cal. 16.1 and 16.3 Hz, respectively. This value is in good agreement with the expected value for a  ${}^{3}J_{\text{trans}}$  coupling of the vinylic protons. Further structural characteristics were confirmed by FT-IR, <sup>13</sup>C NMR and ESI-MS.

# (E)-2-(4-(4-(9H-carbazol-9-yl)styryl) phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (CBZ-OXA-IV):

Colour: Light green colour. Obtained yield: 83%. MP: 210–211 °C. FT-IR (KBr, cm<sup>-1</sup>): 3052 (C-H aromatic), 2955 (C-H aliphatic), 1600 (C = C olefinic), 1547, 1514 (C=C and C=N aromatic), 1227, 1067 (C–O–C asym and C–O–C sym, oxadiazole ring); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.17 (d, *J*=4.2 Hz, 2H), 8.15 (d, *J*=3.3 Hz, 2H), 8.14 – 8.03 (m, 4H), 7.79 (d, *J*=8.6 Hz, 2H), 7.73 (d, *J*=8.5 Hz, 2H), 7.61 (d, *J*=8.6 Hz, 2H), 7.57 (d, *J*=8.7 Hz, 2H), 7.39 (d, *J*=16.3 Hz, 1H), 7.32 (d, *J*=8.0 Hz, 2H), 7.28 (d, *J*=8.5 Hz, 2H), 6.78 (d, *J*=16.1 Hz, 1H), 1.39 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.68, 164.25, 155.41, 140.69, 140.37, 135.86, 131.16, 130.37, 129.88, 129.56, 128.12, 127.26, 127.13, 126.81, 126.10, 126.01, 123.49, 123.01, 121.10, 120.37, 120.10, 109.81, 35.13, 31.12; ESI–MS: m/z [M+H]<sup>+</sup> calculated for C<sub>38</sub>H<sub>31</sub>N<sub>3</sub>O 546 found 546.

# Conclusion

In conclusion, we have designed and synthesized a novel  $\pi$ -conjugated carbazole-1,3,4-oxadiazole-based D- $\pi$ -A type bipolar fluorophore CBZ-OXA-IV. The dye CBZ-OXA-IV emits intense deep blue fluorescence with quantum yields ( $\Phi$ ) 0.40 and large Stokes shifts about 7052 cm<sup>-1</sup>, which is comparable to the reported Cz-OXD dvads having blue emission bands with fluorescence quantum yields in the range of 0.80 to 0.99 [23]. Optical band gap  $(E_g^{opt})$  value of dye CBZ-OXA-IV is 3.01 eV. It is noteworthy that the  $E_{p}^{opt}$  for **CBZ-OXA-IV** is lower than the popular and most often employed host materials, i.e.,  $mCP(\hat{E}_g^{opt} = 3.56\text{eV})$ and CBP  $(E_{g}^{opt} = 3.49 \text{eV})$  [60]. The electrochemical properties of CBZ-OXA-IV dye have been investigated in detail by using cyclic voltammetry (CV) measurements. Interestingly, HOMO/LUMO energy levels of CBZ-OXA-IV dye calculated from the DFT computations were found to be -5.82 and -1.76 eV, respectively, which are good agreement with the HOMO/LUMO energy level values measured using CV to be -5.72 and -2.71 eV, respectively. Almost complete separation of HOMO/LUMO energy levels is efficient for charge carrier transfer and balance in the emitter layers of OLEDs [50], which may endow the fluorophore **CBZ-OXA-IV** with the ability of bipolar charge transport. The glass transition temperatures (Tg) for the compound CBZ-OXA-IV at 98 °C. It is quite interesting to notice that the glass transition temperatures (Tg) of **CBZ-OXA**-IV higher than popular and most often employed host materials in the literature, i.e., mCP (Tg = 60 °C), CBP (Tg = 62 °C), BCz1 (Tg = 67 °C), BCz3 (Tg = 77 °C) and TCz1 (Tg = 88 °C). Also, it is important to mention that the glass transition temperature (Tg) of **CBZ-OXA-IV** is higher than those of the most popular oxadiazole-based electron-transporting materials, such as, 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD, Tg = 60 °C), 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7, Tg = 77 °C) and is higher than the recently reported non-bipolar host-emitters that contain oxadiazoles (BOBP, Tg = 45 °C) [59, 60]. The decomposition temperatures  $(T_{d5\%})$  for the compound **CBZ-OXA-IV** at 387 °C. The obtained overall results demonstrated that the novel bipolar fluorophore CBZ-OXA-IV is a potential candidate for optoelectronics applications and possibly can be applied as bipolar transport materials in the field of optoelectronic devices/OLEDs.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-021-02778-1.

Acknowledgements We are thankful to the University Scientific Instrument Centre (USIC) and SAIF, Karnatak University, Dharwad for providing the spectral data. Also to the University Grants Commission (UGC), New Delhi, India, for providing financial support under UGC-SRF (Sr. No. 2121510180 Ref. No. 20/12/2015) and DST-Purse Phase-II program for providing necessary facilities. The authors, Tilakraj T S is thankful to UGC-JRF for funding (Sr. No. 2061651259 Dated. 26/10/2017) and Mallikarjun K. Patil would like to thank KSTePS Govt. of Karnataka for Providing DST-Ph.D fellowship.

Authors' Contributions Mahesh S. Najare: Conceptualization, design of study and Writing-Original draft preparation. Mallikarjun K. Patil: Acquisition of data and Writing-Original draft preparation. Tilakraj T S: Analysis, interpretation of data and Formal analysis. Mohammed Yaseen: Resources and Software. AfraQuasar A. Nadaf: Data Curation and Validation. Shivaraj Mantur: Analysis and interpretation of data. Sanjeev R. Inamdar: Visualization, Investigation, Reviewing and Editing. Imtiyaz Ahmed M. Khazi: Supervision.

**Funding** No specific funding was received for this project. Mahesh Sadashivappa Najare is supported by a University Grants Commission (UGC), New Delhi, India, under UGC-SRF (Sr. No. 2121510180 Ref. No. 20/12/2015). All authors confirm their work is independent from the funders.

**Availability of Data and Materials** All data generated or analysed during this study are included in supplementary information file.

#### Declarations

**Conflicts of Interest** Authors declare that there are no conflicts of interest.

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