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Novel benzothiadiazine 1,1-dioxide based bipolar host materials for efficient red phosphorescent organic light emitting diodes

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ABSTRACT

In this work, three novel bipolar host materials **TPA-SA**, **3CBZ-SA** and **4CBZ-SA** have been designed and synthesized by incorporating triphenyl amine and carbazole as donor and benzothiadiazine 1,1-dioxide as an acceptor. These molecules exhibit moderately high triplet energies and bipolar carrier transport characteristics (ambipolarity) which is useful for the exothermic energy transfer to the dopants and also for the balanced carrier injection/transport in the emissive layers. These materials exhibited good performances in PhOLEDs and furnished external quantum efficiency in the range of 10.0–15.0%. Notably, a red phosphorescent device using **TPA-SA** as the host doped with **Ir(pq)₂(acac)** exhibited a maximum EQE, power efficiency and current efficiency of 15.0%, 16.0 lm/W, and 25.3 cd A⁻¹, respectively.

1. Introduction

The phenomenon of electroluminescence in organic compound was first observed in acridine orange thin film upon applying high voltage [1]. Subsequently, Tang et al. demonstrated first practical green organic light emitting diode comprised of Tris(8-hydroxyquinolinato) aluminium (Alq₃) sandwiched between a cathode and an anode [2]. Initially, fluorescent organic materials were used as emitting layer, but their internal quantum efficiency could not be extended beyond 25% as per spin statistics rule which limited their applications in display technologies. In fluorescent OLED's only 25% of singlet excitons are utilized while 75% triplet excitons get wasted in the form of heat or other non-radiative decays. As per the spin selection rule, transition from triplet excited state to the singlet ground state is forbidden but use of organometallic complexes comprising heavy metals such as Ir, Pt, Re and Os induces a spin – orbit coupling which opens a radiative path for the transition and promote intersystem crossing [3].

The designing of tailor-made bipolar host materials which contains

balanced charge transport properties is very crucial for making highly efficient phosphorescent organic light-emitting diodes (PhOLEDs) [4]. Moreover, the host material must possess high triplet energy as compared to guest so that reverse energy transfer from the guest back to the host can be prevented and excitons would remain confined on guest molecule. Nevertheless, they should be capable of suppressing the unfavorable effects such as aggregation caused quenching and triplet---triplet annihilation of phosphorescent emitters [5].

In this context, different classes of bipolar host materials have been designed and synthesized with abundant combinations of hole- and electron transporting moieties. Typically, carbazole and arylamine are frequently used as hole-transporting motifs owing to its excellent hole mobilities (μ_h *ca.* 10^{-3} to 10^{-5} cm² V⁻¹s⁻¹) [6] whereas, oxadiazole, triazine, phenanthroline, and benzimidazole are commonly used as electron-transporting moieties [7–13].

More recently, Jia et al. [14] reported two host materials DAMP and DCMP incorporating carbazole and triphenyl amine for hosting green (EQE = 19.5% and 22.2%) and red (EQE = 15.3% and 20.0%)

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phosphorescent OLED's. Two novel bipolar host materials M1 and M2 based on carbazole/diphenyl quinoxaline were synthesized by Gao et al. [15] and tested for red phosphorescent OLEDs and have shown EQE of 14.66% and 15.07% respectively. In addition, Lee et al. [16] designed and synthesized a series of bipolar host materials with dipyridyl amine and carbazole linked to triazine core (p-BCTPy, m-BCTPy and 3-BCTPy) and tested for green PhOLEDs. Amongst three, 3- BCTPy shown relatively high EQE of 18.9%.

This clearly emphasized that carbazole and triphenyl amine are very important moieties in bipolar host molecules owing to its high triplet energy and excellent hole transporting properties. Various electron acceptor units such as pyrrolo[1,2-a]quinoxaline [17], triazolopyridine [18], triazole [19], triazine [20], oxadiazole [21], phosphine oxide [22], etc. were used in combination with carbazole and triphenyl amine to

induce bipolar characteristic in molecules. Albeit, benzothiadiazine 1, 1-dioxide is not explored so far as electron acceptor unit in bipolar host materials. Strong electron accepting nature of sulfone moiety makes them an attractive candidate to be used in bipolar host material as an acceptor unit. In last few years, some reports were published which utilizes sulfone core as an electron acceptor unit to fabricate electroluminescent devices. [23]. Their performance as bipolar hosts are still limited and need to be explored to the full potential. In this context, we here with report synthesis and characterization of novel and high triplet energy bipolar host materials, **TPA-SA**, **3CBZ-SA** and **4CBZ-SA** for the application in red phosphorescent OLED.



Scheme 1. Synthesis of TPA-SA, 3CBZ-SA and 4CBZ-SA.

2. Result and discussion

2.1. Synthesis

Synthetic pathway for the **TPA-SA**, **3CBZ-SA** and **4CBZ-SA** is depicted in Scheme 1. The intermediates **1**, **3** and **4** were synthesized using previously reported methods [24–26]. Intermediate **1** is obtained by the Vilsmeier-Haack reaction on triphenyl amine. Carbazole on *N*-arylation using iodobenzene gave *N*-phenyl carbazole (**2**) which subsequently formylated using DMF/POCl₃ to form **3**. Intermediate **4** was synthesized *via* reaction of carbazole with 4-bromobenzaldehyde in presence of CuI as a catalyst. The condensation reaction of **1**, **3**, and **4** with 2-amino benzenesulfonamide in the presence of sodium bisulphite resulted in the formation of **TPA-SA**, **3CBZ-SA** and **4CBZ-SA**, respectively. The products were purified by trituration in diethyl ether and characterized by ¹H, ¹³C NMR and mass spectroscopy.

2.2. Thermal properties

TPA-SA, **3CBZ-SA** and **4CBZ-SA** exhibited excellent morphological stabilities with decomposition temperatures (T_d) of 394 °C for **TPA-SA**, 412 °C for **3CBZ-SA** and 417 °C for **4CBZ-SA**, corresponding to 5% weight loss, calculated using thermogravimetric analysis (TGA). Glass transition (T_g) and melting temperature (T_m) were determined using differential scanning calorimetry (DSC). **TPA-SA**, **3CBZ-SA** and 4**CBZ-SA** displayed glass transition temperature of 267 °C, 235 °C and 231 °C, and melting temperature of 351 °C, 381 °C and 344 °C, respectively. Such significantly high values of T_g and T_d for these compounds suggests that they can be sublimed using vacuum thermal unit, also they are capable of resisting inevitable joule heating which occur during device operation.Fig. 1.

2.3. Photophysical properties

The electronic absorption (UV–vis) and photoluminescence (PL) spectra (recorded at 298 K) of **TPA-SA**, **3CBZ-SA** and **4CBZ-SA** in various solvents and in the form of solid thin films are depicted in Fig. 2. The data is summarized Table 1. **TPA-SA** showed absorbance at 281–292 nm and 353–373 nm, **3CBZ-SA** displayed absorption peaks in the range of 289–299 nm and 325–341 nm while **4CBZ-SA** exhibited absorption peak at 282–293 nm and 335–358 nm. The solvent polarity independent absorption band from 281 to 299 nm are ascribed to the π - π * transition while peaks in the range of 325–373 nm are due to n- π * transition of the carbazole moiety. The higher wavelength absorption is due to the occurrence of intramolecular charge transfer between carbazole(donor) and benzothiadiazine 1,1-dioxide (acceptor). The

solvent-independent nature of absorbance shows that the Franck-Condon transitions leads to small change in dipole moment at the ground state. The PL spectra in toluene solution were recorded at 298 K. TPA-SA, 3CBZ-SA and 4CBZ-SA shows emission maxima at 470, 396, 434 nm respectively, which correspond to singlet emission. The significant solvent-dependent emission was observed for 3CBZ-SA. The emission spectral shift proportional to solvent polarity suggested rapid photo-induced electron transfer (PET) which led to a noticeable change in the dipole moment in the excited state. Further, red-shifted PL spectra observed for neat film of 3CBZ-SA exhibiting different dielectric surrounding in the solid state. The triplet energies (E_T) of 2.43–2.64 eV were observed for TPA-SA, 3CBZ-SA and 4CBZ-SA from the first phosphorescence emission peak of low temperature PL spectrum recorded at 77 K (Table 1).

2.4. Electronic properties

The electrochemical behavior of TPA-SA, 3CBZ-SA and 4CBZ-SA were probed by using cyclic voltammetry measurements. 3-Electrode cell system encompassing a glassy carbon electrode as working electrode, silver/silver chloride (Ag/AgCl) as reference electrode and a platinum wire as counter electrode was used. Oxidation scans were performed using 0.1 M tetra(n-butyl)ammonium hexafluorophosphate (TBAPF₆) in CH₂Cl₂ and reduction scans were performed using tetra(nbutyl)ammonium perchlorate (TBAP) in DMF as supporting electrolytes. All of these compounds displayed quasi-irreversible oxidation as well as reduction potentials which may be arise due to their triphenylamine, 9H-phenylcarbazole and benzothiadiazine 1,1-dioxide segments, respectively. The oxidation peak potentials observed at 1.15, 1.16 and 1.21 eV (vs. Fc/Fc⁺) for TPA-SA, 3CBZ-SA and 4CBZ-SA, respectively. These values are meticulously associated to the degree of π -conjugation, TPA-SA, 3CBZ-SA impart lower oxidation potentials as compare to 4CBZ-SA. The HOMO energy levels of these bipolar hosts were calculated using HOMO (eV) = - (Eox onset - $E_{Fc/Fc+}$ onset) - 4.80 eV i.e -5.55, -5.56 and -5.61 eV for TPA-SA, 3CBZ-SA and 4CBZ-SA, respectively. While, LUMO energy levels of TPA-SA, 3CBZ-SA and 4CBZ-SA were evaluated using the formula LUMO = HOMO + E_g , where E_g is an optical bandgap, calculated using absorption onset. 3CBZ-SA and 4CBZ-SA exhibited higher values of HOMO energy level compared to N-phenyl carbazole (-5.88 eV) which helps to prevent the formation of exciplexes with neighboring electron donor unit.Fig. 3.

2.5. Theoretical calculations

The geometrical structures of the **TPA-SA**, **3CBZ-SA** and **4-CBZ-SA** molecular systems were optimized by the density functional theory



Fig. 1. TGA (a) and DSC (b) of TPA-SA, 3CBZ-SA and 4CBZ-SA.



Fig. 2. Photophysical properties of TPA-SA, 3CBZ-SA and 4CBZ-SA in various solvents.

Physical properties of TPA-SA, 3CBZ-SA and 4CBZ-SA.

	$(T_{\rm g}/T_{\rm m}/T_{\rm d})/^{\rm o}$ C	$(E_{1/2}^{Ox}/V$	λ_{abs}^{a} sol/nm	$\lambda_{\rm abs}$ film/nm	$\lambda_{\rm PL}^{a}$ sol/nm	$\lambda_{PL} film/nm$	$E_{\rm T}/{\rm eV}$	(HOMO/LUMO/E _g d)/eV
TPA-SA	267/351/394	1.15	362	370	470	530	2.43	-5.55/-2.60/2.95
3CBZ-SA	235/381/412	1.16	353	340	396	450	2.64	-5.56/-2.32/3.24
4CBZ-SA	231/344/417	1.21	340	350	434	500	2.64	-5.61/-2.56/3.05

 $^{\rm a}\,$ In toluene solution (1 \times 10 $^{-5}$ M).



Fig. 3. Cyclic voltammogram of TPA-SA, 3CBZ-SA and 4CBZ-SA.

(DFT) [27]. CAM-B3LYP functional with 6-31 + G(d,p) basis set was employed for the optimization of all the systems. The optimized geometries are taken for the frequency calculation and verified that the obtained structures are minima on the potential energy surface with zero imaginary frequencies. On the basis of the optimized geometry structures the UV–Vis absorption spectral properties in DMSO solvent were calculated by time-dependent density functional theory (TD-DFT) [28] associating with the polarized continuum model (PCM). [29,30]. The calculated plots of the frontier molecular orbitals (HOMO and LUMO) were visualized using the UNIVIS software [31]. All the calculations were performed with GAUSSIAN09 [32] program.

The theoretically calculated λ_{max} of **TPA-SA** in DMSO solvent at CAM-B3LYP/6-31 + G(d,p) level of theory is observed at 329.9 nm with oscillator strength (f) value of 0.98 (See Table 2). For **3CBZ-SA**, the respective λ_{max} and corresponding f values are observed to be 293.4 nm and 0.20, whereas, for **4CBZ-SA**, these values turned out to be 304.1 nm and 0.61 respectively. The corresponding to λ_{max} values in all the three systems are dominated by HOMO to LUMO transitions. The HOMO and LUMO diagrams in Fig. 4 clearly show that the HOMOs of all the molecules are located on donor triphenyl amine or carbazole and the LUMOs are located on benzothiadiazine 1,1-dioxide acceptor parts. This clearly highlights the bipolar nature of the molecules where the intramolecular charge transfer occurs from donating group (triphenyl amine or carbazole) to accepting (benzothiadiazine 1,1-dioxide) ones.

The calculated λ_{max} values of all the three molecules are slightly lower than the respective experimentally observed ones (cf. Table 2). However, the trend of the calculated λ_{max} values correlated well with the respective experimental ones having a correlation coefficient of 0.99 (cf. Fig. 5). The **TPA-SA** shows highest λ_{max} value, whereas, that of the **3CBZ-SA** becomes the lowest one.

The HOMO-LUMO energy gap (E_{HL}) calculated at CAM-B3LYP/6-31 + G(d,p) level of theory are tabulated in Table 2. In comparison with the experimentally obtained energy band gap (E_g) in Table 2, theoretically calculated $E_{\rm HL}$ values are observed to be overestimated. This discrepancy can be attributed to the different platform used to obtain the values. Despite of this, the obtained trend of E_g and $E_{\rm HL}$ is quite similar. The normalized values of $E_{\rm HL}$ to **TPA-SA** i.e. $E_{\rm NHL}$ are matching very well with Eg values.

3. Devices fabrication and EL performance

3.1. Device fabrication and characterization

Before depositing organic layers, Indium-tin-oxide (ITO) glass substrates (sheet resistance ${\sim}15\,\Omega\,{\rm sq}^{-1}$) were cleaned in an ultrasonic bath using deionized water and 2-propanone in succession for 20 min each, followed by warmed in methanol for 10 min. The cleaned ITO glass

Table 2

The calculated maximum absorption wavelength (λ_{max}) value, oscillator strength (f) with respective most probable transition at CAM-B3LYP/6-31 + G(d,p) level of theory along with experimental λ_{max} of the studied compounds in DMSO. E_{HL} is the HOMO-LUMO energy gap, E_{NHL} is the normalized E_{HL} calculated at CAM-B3LYP/6-31 + G(d,p) level of theory and E_g is the experimental band gap.

Systems	Theoretical λ_{max} (nm)	f (Transition)	$E_{\rm HL}$ (eV)	${}^{a}E_{\rm NHL}$ (eV)	Experimental λ_{max} (nm)	^b Eg (eV)
TPA-SA	329.9	0.98 (HOMO	6.044	2.95	358	2.95
		>LUMO)				
3CBZ-SA	293.4	0.20 (HOMO	6.618	3.23	331	3.24
		-LUMO)				
4CBZ-SA	304.1	0.61 (HOMO	6.199	3.03	341	3.05

^a $E_{\rm NHL} = E_{\rm HL}/2.95$, The values of respective HOMO and LUMO energies are given in supporting information Table S3.

^b See Table 1 for details.



Fig. 4. Schematic representations of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) having isosurface value 0.030 a.u. of the studied compounds.



Fig. 5. Graph of maximum absorption wavelength (λ_{max}) value calculated at CAM-B3LYP/6-31 + G(d,p) level of theory against respective experimental one of the studied compounds in DMSO.

substrates were then treated with UV-ozone to remove residual organic contamination. NPB (N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine), TAPC (di-{4-N,N-ditolyl-aminophenyl}cyclohexane) or TCTA (4,4',4"-tris(N-carbazolyl)-triphenylamine) were chosen as the

hole-transporting layer. Ir(pq)₂(acac) (bis(2-phenylquinoline) (acetylacetonate)iridium(III)) was used as the red dopant of the PhOLEDs. TmPyPB (1,3,5-tris[(3-pyridyl)-phen-3-yl]benzene) or TPBi (2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) were chosen as the electron transporting layer. The chemical structures of the materials used for device fabrication are shown in Fig. 6b. All the organic materials were deposited via a vacuum evaporation technique under a base pressure of 1×10^{-6} Torr with a deposition rate of 0.1 nm s⁻¹. Finally, LiF and Al cathodes were deposited without breaking the vacuum at a rate of 0.01 nm $\rm s^{-1}$ and 0.5 nm $\rm s^{-1},$ respectively. The thicknesses of organic layers were acquired with a SOPRA ellipsometer. The current density-voltage-luminance (J-V-L) characteristics of the devices were measured simultaneously in a nitrogen filled glove-box using a Keithley 2400 source meter and a Keithley 6485 picoammeter equipped with a calibrated silicon photodiode. The EL spectra of the devices were recorded using an Ocean Optics QE65000 spectrometer.

3.2. Thin film and device characterization

On the basis of the favorable results from physical study and photophysical investigation it is clear that all the materials possess promising characteristics that can allow them to serve as a host of phosphorescent dopants due to their appropriate HOMO/LUMO energy level and moderate triplet energy. After estimation of the HOMO and LUMO levels of the sulfonamide based materials, we fabricated three PhOLEDs with the following optimized architectures (Fig. 6a): (I) ITO/



Fig. 6. (a) Energy level diagram of materials used in the TPA-SA, 3CBZ-SA and 4CBZ-SA devices; (b) chemical structures of the materials used for device fabrication.

TAPC (60 nm)/**TPA-SA** with 12% $Ir(pq)_2(acac)$ (20 nm)/TPBi (60 nm)/ LiF (0.5 nm)/Al (130 nm); (II) ITO/TAPC (20 nm)/TCTA (20 nm)/**3CBZ-SA** with 12% $Ir(pq)_2(acac)$ (20 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (130 nm); (III) ITO/NPB (40 nm)/TCTA (20 nm)/**4CBZ-SA** with 6% Ir (pq)_2(acac) (20 nm)/TmPyPB (60 nm)/LiF (1 nm)/Al (130 nm).

The current density-voltage-luminance (J-V-L), current efficiencyluminance-power efficiency and EQE-luminance characteristics and the EL spectrum plots for the devices are shown in Fig. 7, and the performance parameters are compiled in Table 5. All devices emit the characteristic red light of $Ir(pq)_2(acac)$, and the EL spectrum is nearly superimposable with the PL spectrum, indicating that light emission originates from $Ir(pq)_2(acac)$. The **TPA-SA** device shows the highest luminance (33484 cd/m²), maximum external quantum efficiency (15.0%) and maximum current efficiency (25.3 cd/A). However, **TPA-SA** device shows lower power efficiency than **4CBZ-SA** due to its higher turn-on voltage. The high turin-on voltage exhibited in the **TPA-SA** device might due to its shallow LUMO level, which make the energy barrier between the emission layer and electron transporting layer slightly higher in the **TPA-SA** device compared to other devices. The high EQE of **TPA-SA** can be attributed to the large spectral overlap between the absorption of $Ir(pq)_2(acac)$ and the emission of **TPA-SA**.

4. Conclusions

In summary, we have designed and synthesized three novel benzothiadiazine 1,1-dioxide based bipolar host materials **TPA-SA**, **3CBZ-SA** and **4CBZ-SA**. All the three materials were used for fabrication of the red phosphorescent OLED and amongst them **TPA-SA** showed good device performance with maximum external quantum efficiency, current efficiency and power efficiency of 15.0%, 25.3 cd/A, 16.0 lm/W,



Fig. 7. (a) Current density-voltage-luminance (J-V-L) characteristics, (b) power and current efficiency, (c) EQE, and (d) emission spectra of the OLED devices for the three compounds.

Table 5

Electroluminescent characteristics of the devices.

Material	V _{turn-on} (V)	L_{max} (cd/m ²)	$\eta_{ext.max}$ (%)	$\eta_{ext@1000cd/m}2$ (%)	$\eta_{c,max}$ (cd/A)	$\eta_{c@1000cd/m}2$ (cd/A)	$\eta_{p.max}$ (lm/W)	$\eta_{p@1000cd/m}2$ (lm/W)
TPA-SA	4.6	33484	15.0	11.9	25.3	20.1	16.0	5.8
3CBZ-SA	2.7	21394	10.0	6.1	15.2	11.3	17.6	6.0
4CBZ-SA	2.9	21429	12.7	8.3	20.6	12.6	22.5	6.2

 $V_{turn-on} = turn-on \ voltage; \\ L_{max} = maximum \ luminance; \\ \eta_{ext.max} = maximum \ external \ quantum \ efficiency; \\ \eta_{ext@1000cd/m}2 = external \ quantum \ efficiency; \\ \eta_{emax} = maximum \ current \ efficiency; \\ \eta_{c@1000cd/m}2 = current \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{p.max} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{cmax} = maximum \ power \ efficiency; \\ \eta_{p@1000cd/m}2 = power \ efficiency \ at \ 1000 \ cd/m^2; \\ \eta_{pmax} = maximum \ power \ efficiency; \\$

respectively. We think that the present study of benzothiadiazine-1,1dioxide based bipolar host materials will open a new avenue for the molecular designing in the area of organic LED's.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2021.106104.

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