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Strategy to improve the efficiency of solution-processed phosphorescent organic light-emitting devices by modified TADF host with tert-butyl carbazole



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ABSTRACT

A new bipolar host material t3Cz-SO was designed and synthesized by introducing tert-butyl carbazole unit to the peripheral of parent TADF units. The calculated triplet energy and ΔE_{ST} of t3Cz-SO are 2.85 and 0.11 eV, respectively. Moreover, t3Cz-SO exhibited excellent film-forming ability and morphological stability, which are suitable for the fabrication of solution-processed OLEDs. The FIrpic-based device host with t3Cz-SO achieved low turn-on voltage of 3.5 V and high power efficiency of 16.5 lm W⁻¹, which is almost ten times higher than the unmodified parent TADF molecule. This study shows that the introduction of tert-butyl carbazole unit to the periphery of small molecular TADF emitter is an effective method for the development of efficient electroluminescent materials.

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1. Introduction

Organic light emitting diodes (OLEDs) have already become the most promising technology in the display field thanks to its advantages such as low energy consumption, self-luminescence, high flexibility and high resolution [1–3]. So far, thermally activated delayed fluorescent (TADF) OLEDs have become a promising alternative for high-efficiency organic light emitting diodes (OLEDs) [4], in which TADF emitters emerge remarkable performance because it has the potential to improve efficiency by fully harvesting singlet and triplet excitons from the triplet (T₁) state to the singlet (S₁) state through reverse intersystem crossing (RISC) process to achieve 100% internal quantum efficiency and avoid the use of expensive heavy-metal [5–7]. Generally, the emission layer (EML) of the solution-processed devices mainly comprise the dopant and host materials [8,9]. Since the optical, electrochemical

** Corresponding author. School of Environmental and Chemical Engineering, Jiangsu Ocean University, Lianyungang, Jiangsu, 222005, China. and electroluminescence properties of the host material directly affect the performance of the devices [10,11], such as turn-on voltage, current efficiency, power efficiency and external quantum efficiency (EQE). The host materials occupy an important position in EML and choosing the proper host materials is the key to controlling the efficiency and brightness of the OLED devices [12–14].

Normally, the host materials for phosphorescent emitters are conventional unipolar electron-transport or hole-transport materials [15], the narrow recombination zone exists near the EML interface, which may cause rapid roll-off of efficiency, which will affects the stability of devices [16,17]. Therefore, the bipolar host molecules, which contain two parts of electron donating (D) and electron accepting (A), come to be more functional. Bipolar host molecules have been shown to facilitate the injection and transport of holes and electrons, widen the recombination zone, and thus mitigate the efficiency roll-off [18–20]. For example, Lee [21] and his group synthesized three triphenylene derivatives for the use as hosts for green PhOLEDs and achieved a high EQE up to 20.3%. Kang [22] and co-workers reported three different host molecules with carbazole, carboline, and DBT moieties in one molecular structure. They have similar T_1 levels, lower driving voltages (4.7–5.0 V),

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significantly higher EQEs than the devices containing an mCP host and an unprecedentedly high EQE of around 25.7%. However, traditional TADF molecules are not conducive to solution-processed devices due to their small molecular structure, easy crystallization, and poor film-forming properties [23]. TADF host molecules used in the preparation of solution-processed OLED devices should meet the following conditions: (a) has good solubility in commonly used organic solvents; (b) has good film-forming properties so that devices can be prepared by spin coating and inkjet [16]; (c) possess higher triplet energies than those of the dopant emitters to prevent reverse energy transfer from the guest back to the host, as well as confine triplet excitons in the emissive layer [22,24].

In this work, we designed and synthesized a new molecule t3Cz-SO, which fully demonstrated that the introduction of tertbutylcarbazole in the periphery of the small molecular TADF molecule can improve the film-forming performance and solubility of the material, while effectively maintaining the TADF properties of the material. Electrochemical studies showed that the introduction of the tert-butylcarbazole group effectively inhibited the self-polymerization of molecules under external stimulus, and after the film was thermally annealed at 150 °C, it still maintained the good spectral performance and morphological stability. Compared with the device made of unmodified molecules, the performance of the device prepared by the host material of blue phosphorescent molecules was significantly improved.

2. Experimental section

2.1. Chemicals

The synthesis of the compounds 3,6-di-tert-butyl-9H-carbazole (1), 3,6-diiodo-9H-carbazole (2), 3,6-diiodo-9-tosyl-9H-carbazole (3), 3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9-tosyl-9H-carbazol -6-yl)-9H-carbazole (4) and 3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H) -carbazol-9-yl)-9H-carbazole (5) were prepared according to published procedures [25]. All chemicals were purchased from Energy Chemistry companies and used without further purification unless otherwise noted. N, N-dimethylformamide (DMF) and methylene chloride (DCM) solvents were dewatered according to standard procedures. The synthetic routes and chemical structures of Cz-SO and t3Cz-SO

are shown in Scheme 1. 2.2. *General method*

¹H and ¹³C NMR spectra are recorded on a BRUKER AMX instrument. Elemental analysis is performed using an Elementar Vario EL CHN elemental analyzer. Molecular masses are measured by a BRUKER DALTONICS matrix-assisted laser desorption ionization time-of-fight mass spectrometer (MALDI-TOF-MS). The UV-vis absorption spectra of the compounds are measured by SHIMADZU UV-2450. The photoluminescence emission spectra are recorded on HORIBA FLUOROMAX-4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves are recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409 PC). Cyclic voltammetry (CV) is performed on a CHI750C voltammetric analyzer in a typical three-electrode cell with a platinum plate working electrode, a platinum wire counter electrode and a silver wire reference electrode. The optimized structure is calculated by Gaussian09 at the B3LYP functional with 6-31G(d) basis sets. The excitation energies in the singlet and triplet states are obtained using the TD-DFT method based on an optimized molecular structure for the ground state.

3. Synthesis

3.1. 9- (4-(phenylsulfonyl)phenyl)-9H-carbazole (Cz-SO)

Bromo-4-(phenylsulfonyl)benzene (0.5 g, 1 mmol), 9H-carbazole (0.31 g, 1.1 mmol), K_2CO_3 (0.7 g, 3 mmol), Cul (0.064 g, 0.2 mmol), 1,10- Phenanthroline hydrate (0.062 g, 0.2 mmol) are added to a 100 mL round-bottom flask, and then N, N- dimethylformamide (DMF, 20 mL) is added under a nitrogen atmosphere. After stirring for 24 h at 110 °C, the reaction mixture is cooled to room temperature. The solvent is removed under reduced pressure and the mixture is extracted with CH₂Cl₂ and ultrapure water. The organic extracts are combined, and dried over NaSO₄. Upon evaporating off the solvent, the crude product is purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ to yield M1 (0.83 g, 61%) as a white powder. ¹H NMR (500 MHz, CDCl₃): δ 8.20–8.15 (m, 2H), 8.12 (d, J = 7.7 Hz, 2H), 8.05–8.02 (m, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.65–7.53 (m, 3H), 7.44–7.35 (m, 4H),



Scheme 1. Synthetic Routes and Chemical Structures of Cz-SO and t3Cz-SO.

7.35–7.27 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 142.47, 141.38, 139.97, 139.75, 133.48, 133.18, 129.57, 129.50, 129.28, 127.86, 127.68, 127.09, 126.33, 123.96, 120.93, 120.54, 109.61.

3.2. 3,6-di-tert-butyl-9H-carbazole (1)

Carbazole (5.016 g, 30 mmol), AlCl₃ (4.0 g, 30 mmol) and CH₂Cl₂ (120 mL) are added to a 100 mL round-bottom flask. After cooling to 0 °C, tert-butyl chloride (7.5 ml 60 mmol) is placed in CH₂Cl₂ (20 ml) and added dropwise for 20 min to form a dark yellow solution. The mixture is stirred at 0 °C for 1 h and at room temperature for 9 h, then pour into ice water and extracted with CH₂Cl₂. The combined organic phase is washed with water, brine, dried over anhydrous NaSO₄, filtered, and concentrated under reduced pressure. The crude product is purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ to yield 1 (0.87 g, 65%) as a white powder. ¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, J = 1.8 Hz, 2H), 7.84 (s, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 1.44 (s, 18H).

3.3. 3,6-diiodo-9H-carbazole (2)

Carbazole (1.00 g, 5.98 mmol), acetic acid (16 mL) are added to a 100 mL round-bottom flask and the solution is heated to 50 °C. Then KI (1.29 g, 7.77 mmol) is added. After stirring for a few minutes, a solution of KIO₃ (1.279 g, 5.98 mmol) in acetic acid (2 mL) is added dropwise. After the mixture is refluxed for 1 h, a light red suspension is obtained. After cooling to room temperature, adding water and extracted with CH₂Cl₂. The obtained organic phase is washed with water, brine, and dried over anhydrous NaSO₄, then filtered, and concentrated. The crude product is purified by column chromatography on silica gel with ethyl acetate/petroleum ether to yield 2 (0.87 g, 65%) as a red-brown powder. ¹H NMR (500 MHz, CDCl₃): δ 8.32 (d, J = 1.8 Hz, 2H), 8.10 (s, 1H), 7.66 (dd, J = 8.2, 1.6 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H).

3.4. 3,6-diiodo-9-tosyl-9H-carbazole (3)

To a solution of 2 (1.5 g, 3.58 mmol) and KOH (0.92 g, 16.4 mmol) in acetone (20 mL) is slowly added p-toluenesulfonyl chloride (3.127 g, 16.4 mmol) in acetone (2 mL). After refluxing for 15 min, the reaction solution is poured into water and extracted with CH₂Cl₂. The obtained organic phase is washed with water and brine, dried over anhydrous NaSO₄, and finally filtered and concentrated. The crude product is purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ to yield 3 (1.23 g, 63%) as a red-brown powder. ¹H NMR (500 MHz, CDCl₃): δ 8.17 (d, J = 1.2 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 2.27 (s, 3H).

3.5. 3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9-tosyl-9H-carbazol-6-yl)-9H-carbazole (4)

Cul (0.29 g, 1.5 mmol), K_3PO_4 (1.592 g, 7.5 mmol), and (±)-trans-1,2- diaminocycl-ohexane (DACH, 0.2 mL, 1.6 mmol) are added to a 100 mL round-bottom flask. Then adding a solution of 3 (1.72 g, 3 mmol) and 1 (1.85 g, 6.6 mmol) in toluene (40 mL). The above mixture is refluxed and stirred for 24 h. After cooling to room temperature, water and CH₂Cl₂ are added for extraction. The obtained organic phase is washed with water and brine successively, and finally dried with anhydrous Na₂SO₄, then filtered and concentrated. The crude product is purified by column chromatography on silica gel with eluent: petroleum ether/CH₂Cl₂ to yield 4 (0.78 g, 56%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.56 (d, J = 8.2 Hz, 2H), 8.14 (d, J = 1.8 Hz, 4H), 8.02 (d, J = 1.6 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.44 (dd, J = 8.8, 1.6 Hz, 4H), 7.28-7.32 (m, 6H), 2.40 (s, 3H), 1.45 (s, 36H).

3.6. 3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-6-yl)-9H-carbazole (5)

KOH (0.13 g, 2.32 mmol) is added to a 100 mL round-bottom flask, and a solution of 4 (1.0 g, 1.14 mmol) in DMSO (6 mL). THF (12 mL) and water (2 mL) is added, then the mixture is stirred and refluxed for 1.5 h. After cooling to room temperature, adding 10% HCl (20 mL), then adding water (10 mL) and methanol (5 mL). After filtration, the precipitate is collected and rinsed with water. The crude product is purified by column chromatography on silica gel with eluent: petroleum ether/CH₂Cl₂ to yield 5 (0.68 g, 76%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.40 (s, 1H), 8.17 (d, J = 4.8 Hz, 6H), 7.66 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 4H), 7.11 (d, J = 8.6 Hz, 4H), 1.45 (s, 36H).

3.7. 3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9-(4-(phenylsulfonyl)phenyl)-9H-carbazol-6-yl)-9H-carbazole (t3Cz-SO)

1-bromo-4-(phenylsulfonyl)benzene (0.2 g, 1 mmol), 5 (0.53 g. 1.1 mmol), K₂CO₃ (0.28 g, 3 mmol), CuI (0.025 g, 0.2 mmol), 1,10-Phenant-hroline hydrate (0.027 g, 0.2 mmol) are added to a 100 mL round-bottom flask, and then DMF (20 mL) is added under a nitrogen atmosphere. After stirring for 24 h at 110 °C, the reaction mixture is cooled to room temperature. The solvent is removed under reduced pressure and the mixture is extracted with CH₂Cl₂ and water. The organic extracts are combined, and dried over Na₂SO₄. The crude product is purified by column chromatography on silica gel with eluent: petroleum ether/ethyl acetate to yield M2 (0.84 g, 62%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.46 (d, J = 8.6 Hz, 2H), 8.29 (d, J = 1.6 Hz, 2H), 8.20 (d, J = 1.2 Hz, 4H), 8.06 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.68 (dd, J = 8.7, 1.8 Hz, 2H), 7.65-7.55 (m, 5H), 7.49 (dd, J = 8.6, 1.6 Hz, 4H), 7.36 (d, J = 8.6 Hz, 4H), 1.50 (s, 36H). ¹³C NMR (126 MHz, CDCl₃) δ 142.82, 142.40, 140.10, 139.98, 139.43, 131.98, 130.17, 127.48, 126.32, 124.77, 123.67, 123.26, 119.54, 116.34, 111.03, 108.99, 77.31, 77.06, 76.80, 53.46, 34.78, 32.06.

4. Result and discussion

4.1. Thermal Properties

The thermal stability of Cz-SO and t3Cz-SO in solid powder state is tested by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as shown in Fig. 1. The TGA curve shows that the decomposition temperatures (T_d, corresponding to 5% weight loss) of Cz-SO and t3Cz-SO are 278 °C and 513 °C, respectively. The high thermal stability indicates that t3Cz-SO has higher thermal stability than Cz-SO. The DSC curve exhibits that the glass transition temperature (T_g) of Cz-SO is 152 °C, while t3Cz-SO has no obvious glass transition temperature in the range of 25–200 °C. This means that t3Cz-SO will not undergo any morphological changes during the annealing process, which is more advantageous to the spin-coating method for preparing OLED devices.

In order to further verify the film-forming ability of the compounds and the morphologies of the solution-processed films, the atomic force microscopy (AFM) measurement was tested under non-contact mode. The Cz-SO and t3Cz-SO are prepared with 1, 2dichloroethane solution (10 mg/mL), then spin-coated on the ITO/ PEDOT: PSS substrate at a speed of 2000 rpm. Fig. 2 shows the measured surface morphology of these two compounds after spin-



Fig. 1. TGA curves of Cz-SO and t3Cz-SO. (inset) Corresponding DSC traces.

coating. It can be seen from the pictures under the microscope that Cz-SO is not uniformly coated on the surface of the substrate, and there are numerous cracks and blank areas, indicating that the solubility and film-forming ability of Cz-SO are poor. In contrast, the t3Cz-SO film is very smooth and uniform, without any pinholes and cracks. which is a prerequisite for preparing high efficiency solution-processed devices [26]. Therefore, the introduction of tertbutylcarbazole groups on the periphery of carbazole is an effective way to improve the performance of solution processing of traditional small molecule TADF materials. In addition, the roughness value (RMS) of t3Cz-SO in the range of $5 \times 5 \,\mu\text{m}$ measured by AFM is 0.35 nm, which is lower than that of Cz-SO (0.63 nm). The excellent film-forming properties and low film roughness indicate that t3Cz-SO is more conducive to the preparation of solution-processed OLED devices.

4.2. Photophysical Properties

The optical properties of the TADF emitters are obtained using the ultraviolet-visible absorption and photoluminescent (PL) spectra in toluene solution (Fig. 3a). The absorption peaks of both compounds at around 300 nm can be attributed to the π - π * transition absorption of carbazole while the peak around 350 nm can be attributed to the intramolecular charge transfer (ICT) of the D-A system formed between the electron-donating and electronwithdrawing group. The initial wavelength of the absorption spectra of Cz-SO and t3Cz-SO are 367 nm and 406 nm, respectively. Therefore, the optical energy gaps of the Cz-SO and t3Cz-SO are estimated to be 2.79 and 2.52 eV according to the absorption edges. The emission peaks of Cz-SO and t3Cz-SO in toluene solution are located at 397 nm and 440 nm, respectively. Indicating that the introduction of the tertbutyl-carbazole group improved the electron donating properties of the donor group, and making the spectrum red-shifted. However, the emission spectra in the congested film state are significantly influenced that the emission peaks of Cz-SO and t3Cz-SO are 424 nm and 446 nm, respectively. Moreover, Cz-SO and t3Cz-SO in the film state have different degrees of red-shift compared to the solution state, which is caused by the π - π accumulation in the solid state [27]. Furthermore, from solution to solid film state, Cz-SO red-shifts 27 nm, while t3Cz-SO only red-shifts 6 nm, which illustrated that the access of tertbutylcarbazole inhibits the aggregation of molecules in the solid state effectively and improves the luminous efficiency of the material (see Fig. 4).

The emission spectra in different solvents (petroleum ether, toluene, THF, acetone, DMSO, 10^{-3} mol/L) are determined that the emission spectra of the compounds show significant solvent polarity dependence, and the emission peak has a large red-shift with the increase of the solvent polarity. This is because both Cz-SO and t3Cz-SO contain strong electron-withdrawing and electron-donating group to undergo obvious ICT effect after excitation. Thus, as the polarity of the solvent increases, the emission peaks red-shift.



Fig. 2. AFM topographic images of Cz-SO and t3Cz-SO.



Fig. 3. (a) UV-vis absorption and PL emission in toluene solution; (b) PL spectra in film state.



Fig. 4. PL and UV spectra of Cz-SO (a,c) and t3Cz-SO (b,d) in difffferent solvents.

In order to probe the phenomena, a Lippert-Magada diagram is constructed, as shown in Fig. 5. Which expresses the Stokes shift as a function of the solvent polarity parameter $\Delta f(\varepsilon, n)$.

$$\Delta \nu = \nu_{abs} - \nu_f \cong \frac{2(\Delta \mu)^2}{hca^3} \Delta f(\varepsilon, n) + A \tag{1}$$

Where $\Delta f(\varepsilon, n)$ is obtained by the following formula:

$$\Delta \mathbf{f}(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$
(2)

Here, h is the Planck's constant, c is the velocity of light, v_{abs} and v_f are the absorption wavelength and emission wavelength, respectively. $\Delta \mu$ means the difference between the dipole moments of the ground state and the excited state, e represents the static

dielectric constant, and a is Onsanger Radius, C is a constant and n represents the refractive index of the solvent [28]. Related spectral data are listed in Table 1. According to formula (2), the Δf of different solvents can be calculated as Δf (petroleum ether) = 0.001, Δf (toluene) = 0.013, Δf (THF) = 0.210, Δf (acetone) = 0.162, Δf (DMSO) = 0.286 (see Table 2).

From the data in the table, the plots of Δf as a function of Δv with the slope values can be calculated to be 21246 and 14457 cm⁻¹ for Cz-SO and t3Cz-SO (Fig. 5). Accordingly, the calculated $\Delta \mu$ values are 13.64 D and 11.25 D. These results suggest that the ICT effect of t3Cz-SO is weaker than Cz-SO, which contributes to the spectral stability in OLED devices. Besides, we test the photoluminescence spectra of the materials in a certain volume of mixed solvent (10⁻⁵ mol/L) with different volume ratios of THF and water so as to explore the luminescence properties of the materials in the aggregated state. As shown in Fig. 6. Apparently, the luminous



Fig. 5. Lipperte-Mataga plot of Cz-SO and t3Cz-SO in various solutions.

Table 1

Spectral properties of Cz-SO and t3Cz-SO in different solvents.

intensity of both compounds increases with the volume fraction (F_w) of water gradually increasing from 0 to 90%, which means that Cz-SO and t3Cz-SO have the characteristics of aggregation-induced luminescence enhancement.

4.3. Electrochemical properties

Using tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte, the electrochemical characteristics of the two compounds are studied by CV with CH_2Cl_2 for anodic sweeping. Fig. 7 (a) (c) show that both compounds have obvious oxidation behaviors, which means that they have the potential in bipolar carrier transporting. Based on the formula ($E_{HOMO} = -4.75 - E_{ox}$), we calculate the highest occupied molecular orbital (HOMO) energy values of Cz-SO and t3Cz-SO to be -5.65V and -5.62V, respectively. And it is basically consistent with the theoretically calculated values. Fig. 7b (d) show the cyclic voltammetric curves of Cz-SO and t3Cz-SO in CH₂Cl₂ measured at room temperature for scanning 20 times. It can be seen from the figures that after 20 times of continuous scanning, the curve of Cz-SO appears

		SO-Cz			SOCz-2tBuCz		
solvents	$\Delta_{f}^{a}(\varepsilon,n)$	$\lambda_{abs}^{b}(nm)$	$\lambda_{f}^{c}(nm)$	$\Delta v^{d} (cm^{-1})$	$\lambda_{abs}^{b}(nm)$	$\lambda_{f}^{c}(nm)$	$\Delta v^{d} (cm^{-1})$
n-hexane	0.001	249, 295, 335	363	2303	296, 348	414	4581
toluene	0.013	292, 338	388	3813	300, 348	440	6008
THF	0.210	258, 291, 325	458	8935	253, 298, 348	477	7771
acetone	0.162	292, 324	427	7445	293, 348	492	8410
DMSO	0.286	292, 327	442	7957	299, 349	518	9348

^a Δf is the orientation polarizability parameter of the solvent.

^b λ_{abs} is absorption wavelength.

^c λ_{f} is fluorescent wavelength.

^d ΔV is the Stokes shift.

Table 2

Physical properties of Cz-SO and t3Cz-SO.

	T_d/T_g^a (°C)	HOMO/LUMO ^d (eV)	λ _{ab} ^b (nm)	λ _f ^b (nm)	λ _f ^c (nm)	ΔE_{ST} (eV)	S_1/T_1^e (eV)
Cz-SO	278/152	-5.62/-1.55	292, 338	388	424	0.41	3.54/3.13
t3Cz-SO	513/-	-5.08/-1.72	300, 348	440	446	0.11	3.02/2.91

^a Corresponding to 5% weight loss.

^b Measured in CH₂Cl₂ solutions.

^c Measured in neat film.

^d Determined using cyclic voltammetry.

^e Obtained from Gauss simulation.

displacement, while the curve of t3Cz-SO is relatively stable. Therefore, t3Cz-SO has stronger stability under continuous voltage and is more suitable for device preparation.

4.4. Density functional theory simulation

To systematically evaluate the influence of molecular structure on charge properties, the molecular conformation of Cz-SO and t3Cz-SO are optimized at the B3LYP/6-31G level by using Gaussian 09 program, and density functional theory (DFT) calculations are



Fig. 6. PL spectra of Cz-SO and t3Cz-SO in mixed solvents with different volume ratios of THF and water.



Fig. 7. (a) (c) Cyclic voltammograms of Cz-SO and t3Cz-SO measured at room temperature in CH₂Cl₂; (b) (d) Cyclic voltammograms of Cz-SO and t3Cz-SO measured at room temperature in CH₂Cl₂ with scanned 20 times.



Fig. 8. DFT calculations of the molecular configurations in the ground states.

carried out on their molecular energy levels. As shown in Fig. 8, the lowest unoccupied orbital (LUMOs) of the two compounds are mainly centered on the acceptor group of diphenyl sulfone, the highest occupied orbital (HOMO) of Cz-SO is distributed on the carbazole group, while t3Cz-SO is located on the tricarbazole group. Simultaneously, HOMO and LUMO have a small amount of overlap, which would lead to an effective reversed inter-system crossing

(RISC) process and achieve a relatively small ΔE_{ST} and higher PLQY. Moreover, the theoretically calculated HOMO/LUMO energy levels of Cz-SO and t3Cz-SO are -5.62 eV/-1.55 eV and -5.08 eV/-1.72 eV, respectively. Clearly, the HOMO energy level of t3Cz-SO is 0.54 eV higher than Cz-SO, while the LUMO energy is slightly shifted down (0.17 eV). Therefore, the electron donating ability of t3Cz-SO is stronger than Cz-SO. In addition, time-dependent density functional theory (TD-DFT) is performed to calculate the excited state energy that the S₁ levels of Cz-SO and t3Cz-SO are 3.54 eV and 3.02 eV, respectively, and the T₁ levels are 3.13 eV and 2.91 eV. Thus, the ΔE_{ST} of 0.41 eV and 0.11 eV was achieved for the two molecules. Obviously, comparing with Cz-SO, t3Cz-SO has a smaller ΔE_{ST} value, which would lead to an effective reversed intersystem crossing (RISC) process to achieve delayed fluorescence characteristics.

4.5. Electroluminescent Properties

To estimate the applicability of the two materials as solutionprocessed bipolar hosts, we examine the performance of FIrpicbased single-layer blue electro-phosphorescence devices with the simple configuration of ITO/PEDOT: PSS (40 nm)/host: FIrpic (1 wt %, 60 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). Where ITO serves as the anode, PEDOT and TPBI are used as the hole injection layer and electron injection layer, respectively. LiF is used as the electron transport layer, and Al serves as the cathode. A represents the device with Cz-SO as the host material, while B is the device with t3Cz-SO as the host, and the structure and relative energy level are shown in Fig. 9.

The electroluminescence spectrum, current density-voltageluminance (J-V-L) curve, the curves of luminous and power efficiency versus brightness are shown in Fig. 10, and the detailed data of the devices are summarized in Table 3. Both devices show typical blue emission at around 475 nm that originates from the guest, and the emission spectra of the devices are all typical FIrpic emission peaks, indicating a complete energy transfer from the bipolar host to the gust. Among them, the device A displays a turn-on voltage of 4.0 V, a maximum luminous efficiency of 3.82 cd A^{-1} , and a maximum power efficiency of 1.75 lm W^{-1} . In contrast, device B with t3Cz-SO as host reveals a turn-on voltage of 3.5V, a maximum luminous efficiency of 19.94 cd A⁻¹, and the maximum power efficiency of 13.03 lm W^{-1} due to the ΔE_{ST} is smaller. These results consist with the thermal and optical results. Since t3Cz-SO introduces the tert-butylcarbazole group on Cz-SO, the molecular weight increases, and performing more excellent film-forming ability and smaller roughness. Currently, in the process of fabricating solution-processed devices, the flatness of the film has a decisive influence on the stability and efficiency of the device, and different annealing temperatures are required according to the diverse boiling point and volatility of different solvents. Notably, the annealing temperature during the device fabrication is generally high, which means that the better thermal and morphological stability of t3Cz-SO ensure the high device property of the solutionprocessed devices. In addition, the bulky spatial structure of t-butyl effectively inhibits the aggregation induced exciton quenching of t3Cz-SO, which also play a key role of the high device performance.

5. Conclusion

In summary, a simple peripheral modification by introducing tri-tert-butylcarbazole group to the small molecule TADF material is denmostrated to be an effective strategy to obtain efficient TADF host material. the t3Cz-SO has higher morphological stability and enhance film forming ability to enable the fabrication of solution-processed OLEDs. Calculated triplet energy of the two compounds are 397 nm and 440 nm, which are higher than the blue emitter Flrpic to suppress the back energy transfer. Moreover, the ΔE_{ST} of t3Cz-SO is 0.11 eV, which is much smaller than Cz-SO. Both compounds show aggregation-induced luminescence in a mixed solvent of THF and water. Thanks to the excellent photophysical property, the device based on t3Cz-SO achieves a turn-on voltage of 3.5 V, the maximum luminous efficiency of 19.94 cd A^{-1} , the



Fig. 9. The energy diagram of the devices and the molecule structures.



Fig. 10. (a) Current density (hollow)–voltage (J-V)curves; (b) voltage–luminance (solid) (V–L) curves; (c) Current efficiency (hollow) as a function of current density; (d) Power efficiency (solid) as a function of current density; (e) EL spectra of the devices.

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Device performances of the devices.

Device	Host	$V_{on}^{a}(V)$	CE_{max}^{b} (cd A ⁻¹)	PE_{max}^{c} (lm W ⁻¹)	L_{max}^{d} (cd m ⁻²)
A	Cz-SO	4.0	3.82	1.75	3540
B	t3Cz-SO	3.5	19.94	13.03	15320

^a Turn-on voltage at 1 cd m⁻².

^b Maximum current efficiency.

^c Maximum power efficiency.

^d Maximum luminance.

maximum power efficiency of 13.03 lm W^{-1} , and the maximum luminance of 15320 cd m^{-2} , which is higher than the small molecular Cz-SO. This research demonstrates that the introduction of tertiary carbazole units on the basis of the Cz-SO is an effective method for developing high-efficiency electroluminescent materials.

Notes

The authors declare no competing financial interest.

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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