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# Thermally Activated Delayed Fluorescence Materials based on 3,6-Di-*tert*-butyl-9-((phenylsulfonyl)phenyl)-9*H*-carbazoles

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#### **Abstract:**

A series of bipolar materials for thermally activated delayed fluorescence based on 3,6-di-*tert*-butyl-9-((phenylsulfonyl)phenyl)-9*H*-carbazoles, is synthesized by Ulmann coupling reactions. In these materials, the 3,6-di-*tert*-butylcarbazole group is linked at the 3-, 4- position or 3'-, 4'- position of diphenyl sulfone. The effects of the conjugation connectivity on the electronic, photophysical and electrochemical properties of these materials, are studied by extensive UV-vis, fluorescence spectroscopic measurements, cyclic voltammetry and theoretical calculations as well as X-ray crystallographic analysis. The energy gap between singlet and triplet in these materials is tuned from 0.39 eV to 0.22 eV by manipulation of conjugation of the electron donor units.

**Keywords:** carbazole, sulfone, phosphorescence, bipolar,  $\Delta E_{ST}$ , TADF

# **1. Introduction**

High-efficiency organic light emitting diodes (OLEDs) have attracted major interest due to their potential for solid-state lighting and flat panel display applications [1-5]. In recent years, great advances have been made in the development of materials for OLEDs [6-13]. These materials have the potential to lead to cost-effective, light-weight and large area OLEDs. Among them, the energy gap between singlet and triplet ( $\Delta E_{ST}$ ) of the materials plays an important role in realization of high performance OLEDs. Xu et al reported a series of ambipolar ternary hosts with high triplet excited energy and small  $\Delta E_{ST}$  less than 0.4 eV for low-voltage-driving high-efficiency blue PhOLEDs [7]. Duan et al reported bipolar host with  $\Delta E_{ST}$  of only 0.11 eV for low-voltage-driving green OLEDs [11]. To enhance the performance of fluorescence-phosphoresce (F-P) hybrid white organic light emitting diode (WOLED), Zhang et al reported two efficient blue fluorophors with sufficiently small  $\Delta E_{ST}$  to sensitize green and red phosphors [14]. Due to high cost, pollution, low solubility and poor long-term stability of traditional phosphors based on rare metals such as Ir(II), Pt(II), or Os(II), the development of low cost substitutes has attracted more and more attention [15-18]. In principle, when  $\Delta E_{ST}$  is small, reverse intersystem crossing (ISC) can take place [19]. On the basis of this concept, a series of efficient thermally activated delayed fluorescence (TADF) materials as substitutes of phosphors based on rare metals for high-efficiency OLEDs were designed and synthesized [20-29]. In particular, the PhOLEDs based on dicyanobenzene derivatives with a small  $\Delta E_{ST}$  of 0.083 eV show a high external electroluminescent efficiency of 19% [3].

Generally, a small spatial overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is important to achieve a small  $\Delta E_{ST}$ . This task is mostly solved by a design of compounds based on intramolecular charge transfer (ICT). In an ICT based compound, the HOMO and LUMO would be localized at the donor (D) and acceptor (A)

moieties, respectively. Thus, the HOMO and LUMO are well separated, leading to a small  $\Delta E_{ST}$ . In the last few years, various materials with a small  $\Delta E_{ST}$  are designed and applied to OLEDs. Very recently, Adachi et al reported an ICT based molecule with an  $\Delta E_{ST}$  of 0.003 eV, in which the HOMO and LUMO are ideally separated which gave a  $\Delta E_{ST}$  of almost zero [30]. The PhOLEDs based on these molecules show a high external electroluminescent efficiency of 14%. Although various materials for TADF with small  $\Delta E_{ST}$  have been reported as summarized above, there are few systematic studies focusing on the effects of structure on fundamental properties, such as the optical and electrochemical properties particularly the  $\Delta E_{ST}$ .

Recently, a sulfone-containing material attracted major interest for high-efficiency OLEDs because a sulfone moiety possesses a strong electron-accepting nature. Some sulfone based materials have been applied to realize high-performance OLEDs as a host, an electron transporter, or an emitter [31-39]. Kido et al developed a novel high triplet energy host material with a sulfone and *m*-terphenyl moieties for phosphorescent OLED. The performances of blue and green OLEDs using such a system as a host material are the highest levels in the scientic literature [33]. Zhang et al reported two novel blue-violet emitting materials based on a D- $\pi$ -A structural strategy incorporating carbazole as a mild electron-donor and sulfone as an electron-acceptor with a

 $\pi$ -conjugation-breaking feature. The two compounds exhibit high-effciency uorescent emissions with impressively high quantum yields in both solution and film states. The nondoped devices based on these compounds achieved excellent current/power effciencies up to 1.89 cd A<sup>-1</sup>/1.58 lm W<sup>-1</sup> and CIE below 0.06 Adachi developed diphenyl [36]. al sulfone derivative, et a bis(4-(3,6-di-tert-butylcarbazole)phenyl)sulfone (3a) (Scheme 1) as an emitter for blue OLEDs. 3a possesses a  $\Delta E_{ST}$  of 0.32 eV and the corresponding blue OLED achieved a high external

electroluminescent efficiency of 10% [27].

In this context, we became interested in the carbazole/sulfone derivatives, in which the number and position of a 3,6-di-tert-butylcarbazole unit are systematically changed while fixing the central sulfone diphenyl backbone. Here, synthesis, structural features we report the of 3,6-di(*tert*-butyl)-9-((phenylsulfonyl)phenyl)-9H-carbazoles (1a-5a, Scheme 1). The thermal, electronic, photophysical properties of **1a-5a** were explored by extensive thermogravimetric analysis, UV-vis, fluorescence spectroscopic measurements, cyclic voltammetry (CV) and theoretical calculations as well as X-ray crystallographic analysis. The energy difference between singlet and triplet ( $\Delta E_{ST}$ ) in TC-DPSs is tuned from 0.39 eV to 0.22 eV by manipulation the number and position of 3,6-di-tert-butylcarbazole unit.

# 2. Experimental

#### 2.1 General

All reactants and solvents were purchased from commercial sources and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX300 NMR spectrometer with Si(CH<sub>3</sub>)<sub>4</sub> as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Mass spectra were obtained using a Thermo Electron Corporation Finnigan LTQ mass spectrometer. UV-vis absorption spectra were recorded with a spectrophotometer (Agilent 8453) and PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The transient photoluminescence decay characteristics of **1a-5a** in toluene were recorded using a spectrofluorometer (Floromax-4, Horiba). The fast decay component was recorded with a 350 nm LED excitation source, while the slow decay component was recorded with a flash lamp source. Thermogravimetric analysis (TGA) was performed using a Netzsch

simultaneous thermal analyzer (STA) system (STA 409PC) under a dry nitrogen atmosphere at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. Cyclic voltammetry measurements were performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH<sub>2</sub>Cl<sub>2</sub> solutions (10<sup>-3</sup> M) at a scan rate of 100 mV s<sup>-1</sup> with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1M) and ferrocene was selected as the internal standard. The solutions were bubbled with a constant argon flow for 10 min before measurements.

**X-ray crystallography:** X-ray crystallographic analysis of **1a** were performed on a Nonius CAD-4 single-crystal diffractometer by using Mo $K_a$  radiation ( $\lambda = 0.71073$  Å) with an  $\omega/2\theta$  scan mode at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares procedures on  $F^2$  using SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. The isotropic temp. factors were fixed to 1.2 times (1.5 times for CH<sub>3</sub> groups) the equivalent isotropic displacement parameters of the C-atom the H-atom is attached to. Drawings were produced using Diamond 3.0 and Mercury 1.4.1 software. CCDC 973776 (**1a**) contains supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. ccdc. cam. ac. uk/data request/cif.

DFT calculations of **1a-5a** were performed using the Gaussian 03 program package. The calculations were optimized at the B3LYP/6-31G(d) level of theory. The molecular orbitals were visualized using Gaussview [40].

#### 2.2 Synthesis of 1a-e

#### Synthesis of 4-bromo-diphenylsulfone (1b)

To a solution of bromobenzene (3.14 g, 20.0 mmol) and benzenesulfonyl chloride (3.53g, 20.0 mmol) in CHCl<sub>3</sub> (40 mL) was added aluminum chloride (2.67g, 20.0mmol). The reaction mixture was heated under reflux for 24h, the resulting mixture was cooled to room temperature and then poured into 40ml water and extracted with  $CH_2Cl_2$  (2×40 mL). The combined organic phase was then washed with saturated aqueous NaCl solution (2×20 mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **1b** as a white crystal. Yield: 69.54%. M.p.:109-110 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 7.94-7.91 (t, J=7.2Hz, 7.2Hz, 2H), 7.81-7.79 (d, J=5.7Hz, 2H), 7.65-7.48 (m, 5H).

## Synthesis of 3-bromo-diphenylsulfone (2b)

To a solution of dipenylsulfone (10.9 g, 50.0 mmol) in 50 mL of H<sub>2</sub>SO<sub>4</sub> was added *N*-bromosuccnimide (8.9 g, 50.0 mmol) in fractions. The reaction mixture was stirred at 70 °C for 2 h, the resulting mixture was cooled to room temperature and then poured into ice-water (100 mL). The white precipitate was filtered and dried. The crude product was recrystallized from ethanol to produce **2b** as a white solid. Yield: 86.59%. M.p.:90-91 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.08 (s, 1H), 7.96-7.94 (d, J=7.5Hz, 3H), 7.61-7.50 (d, 5H).

#### Synthesis of di(3-bromophenyl)sulfone (4b)

To a solution of dipenylsulfone (10.9 g, 50.0 mmol) in  $H_2SO_4$  (50 mL) was added *N*-bromosuccnimide (17.8 g, 100 mmol) in fractions. The reaction mixture was stirred at 100 °C for 2 h, the resulting mixture was cooled to room temperature and then poured into ice-water (100 mL).

The white precipitate was filtered and dried. The crude product was recrystallized from ethanol to produce **4b** as a white crystal. Yield: 0.60 g (58.08%). M.p.:98-100 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.07(s, 2H), 7.88-7.86 (d, J=7.8Hz, 2H), 7.73-7.71 (d, J=7.8Hz, 2H), 7.40-7.38 (t, J=7.8Hz, 8.1Hz, 2H).

#### Synthesis of di(4-bromophenyl)sulfide (3c)

To a solution of 4-bromoiodobenzene (5.64 g, 20.0 mmol), 4-bromothiophenol (3.78 g, 20 mmol) 1,10-phenanthroline monohydrate (0.8 g, 4 mmol) in DMSO (40 mL) was added K<sub>2</sub>CO<sub>3</sub> (5.52 g, 40 mmol). The reaction mixture was then purged with nitrogen for ten minutes before adding Cu<sub>2</sub>O (0.144 g, 1 mmol). After heated under reflux for 24h under nitrogen, the resulting mixture was cooled to room temperature and then poured into water. The pale precipitate was filtered and dried. The crude product was recrystallized from hexane to produce **3c** as a white crystal. Yield: 66.57%. M.p.:111-112 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.45-7.41 (m, 4H), 7.22-7.16 (m, 3H), 7.65-7.48 (m, 5H) [36].

#### Synthesis of di(4-bromophenyl)sulfone (3b)

To a solution of 30 mL H<sub>2</sub>O<sub>2</sub> (30%, g/g) and 30 mL of HOAc was added **3c** (3.44 g, 10 mmol) in fractions. After heated under reflux for 24h, the resulting mixture was cooled to room temperature and then poured into water. The white precipitate was filtered and dried. The crude product was recrystallized from ethanol to produce **3b** as a white solid. Yield: 84.66%. M.p.:173-174 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 7.80-7.77 (d, J=8.7Hz, 4H), 7.67-7.64 (d, J=8.7Hz, 4H) [36].

### Synthesis of 3, 4'-dibromo-diphenylsulfide (5c)

A procedure similar to that used for **3c** was followed but with 3-bromoiodobenzene instead of 4-bromoiodobenzene. After heated under reflux for 24 h under nitrogen, the resulting mixture was

cooled to room temperature and then poured into water. The mixture was extracted with dichloromethane (3×20 mL). The combined organic phase was then washed with saturated aqueous NaCl solution (2×10 mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **5c** as a white solid. Yield: 58.08%. M.p.:64-65 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 7.49-7.43 (m, 3H), 7.39-7.36 (d, J=7.5Hz, 1H), 7.27-7.14 (m, 4H).

#### Synthesis of 3, 4'-dibromo-diphenylsulfone (5b)

A procedure similar to that used for **3b** was followed but with **5c** instead of **3c**.Yield: 78.08%. M.p.:140-141 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>): δ(ppm) 8.05 (s, 1H), 7.86-7.78 (t, J=7.8Hz, 8.1Hz, 8.4Hz, 3H), 7.71-7.64 (d, J=10.5Hz, 8.7Hz, 3H), 7.41-7.36 (d, J=7.8Hz, 8.1Hz, 1H).

# Synthesis of 3,6-di-tert-butyl-9-(4-(phenylsulfonyl)phenyl)-9H-carbazole (1a)

To a solution of **1b** (0.594 g, 2.0 mmol), 18-crown-6 (0.027g, 0.1 mmol) and 3,6-di-*tert*-butylcarbazole (0.68g, 2.4 mmol) in tetrahydro-1,3-dimethyl-2(1*H*)pyrimidine (DMPU) (5 mL) was added K<sub>2</sub>CO<sub>3</sub> (0.55g, 4.0 mmol). The reaction mixture was then purged with nitrogen for ten minutes before adding CuI (0.020 g, 0.1 mmol). The mixture was stirred at 170°C for 24h under nitrogen, the resulting mixture was cooled to room temperature and then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×20 mL). The combined organic phase was then washed with saturated aqueous NaCl solution (2×10 mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **1a** as a white solid. Yield: 65.01%. M.p.:276-279 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.16-8.11 (m, 4H), 8.06-8.04(d, J=6.6Hz, 2H), 7.75-7.72(d, J=8.4Hz, 2H), 7.63-7.58 (m, 3H), 7.47-7.44 (t, J=8.7Hz, 1.8Hz, 2H), 7.40-7.37 (d, J=8.7Hz, 2H), 1.45 (s, 18H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)

143.7, 142.6, 141.1, 138.6, 137.9, 133.0, 129.1, 129.1, 127.4, 126.1, 123.7, 123.6, 116.1, 108.8, 34.4, 31.6. MS (MALDI-TOF) [m/z]: calcd for C<sub>32</sub>H<sub>33</sub>NO<sub>2</sub>S, 495.22; found, 495.3912. Anal. Calcd. for C<sub>32</sub>H<sub>33</sub>NO<sub>2</sub>S (%): C, 77.54; H, 6.71; N 2.83; S, 6.46. Found: C, 77.40; H, 6.78; N 2.88; S, 6.47.

# Synthesis of 3,6-di-tert-butyl-9-(3-(phenylsulfonyl)phenyl)-9H-carbazole (2a)

A procedure similar to that used for **1a** was followed but with **2b** (0.594 g, 2.0 mmol) instead of **1b**. Yield: 55.48%. M.p.:189-191 °C. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.16-8.12 (d, J=8.7Hz, 1.5Hz, 3H), 8.01-7.99 (d, J=6.9Hz, 3H), 7.81-7.72 (m, 3H), 7.70-7.55 (m, 3H), 7.48-7.44 (t, J=4.8Hz, 6.9Hz, 2H), 7.30-7.28 (d, J=8.4Hz, 2H), 1.47 (s, 18H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 143.4, 143.2, 140.9, 139.1, 138.1, 133.1, 130.4, 130.4, 129.1, 127.5, 125.0, 124.9, 123.6, 116.1, 108.4, 34.4, 31.6. MS (MALDI-TOF) [m/z]: calcd for C<sub>32</sub>H<sub>33</sub>NO<sub>2</sub>S, 495.22; found, 495.4332. Anal. Calcd. for C<sub>32</sub>H<sub>33</sub>NO<sub>2</sub>S (%): C, 77.54; H, 6.71; N 2.83; S, 6.46. Found: C, 77.48; H, 6.79; N 2.87; S, 6.48.

# Synthesis of bis(4-(3,6-di-tert-butylcarbazole)phenyl)sulfone (3a)

To a solution of **3b** (0.376 g, 1.0 mmol), 18-crown-6 (0.027g, 0.1mmol) and 3,6-di(*tert*-butyl)carbazole (0.68g, 2.4 mmol) in DMPU (5 mL) was added K<sub>2</sub>CO<sub>3</sub> (0.55g, 4.0 mmol). The reaction mixture was then purged with nitrogen for ten minutes before adding CuI (0.020 g, 0.1 mmol). The following procedure was similar to that used for **1a**. Yield: 58.21%. M.p.:367-370 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.26-8.23 (d, J=8.4Hz, 4H), 8.13 (s, 4H), 7.83-7.80 (d, J=8.4Hz, 2H), 7.50-7.43 (m, 8H), 1.46 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 143.7, 142.8, 138.4, 137.9, 129.2, 126.2, 123.7, 123.6, 116.1, 108.8, 34.4, 31.6. MS (MALDI-TOF) [m/z]: calcd for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S, 772.41; found, 772.5745. Anal. Calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S (%): C, 80.79; H, 7.30; N 3.62; S, 4.15.found:C, 80.62; H, 7.38; N 3.67; S, 4.17.

#### Synthesis of bis(3-(3,6-di-tert-butylcarbazole)phenyl)sulfone (4a)

A procedure similar to that used for **3a** was followed but with **4b** (0.376 g, 1.0 mmol) instead of **3b**.Yield: 67.26%. M.p.:304-305 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.22 (s, 2H), 8.11-8.10 (d, J=2.1 Hz, 4H), 8.03-8.00 (d, J=7.8Hz, 4H), 7.85-7.82 (d, J=8.4 Hz, 2H), 7.78-7.73 (t, J=8.4Hz, 8.4 Hz, 2H), 7.39-7.36 (t, J=1.8Hz, 6.9Hz, 1.8Hz, 4H), 7.37-7.28 (d, J=8.7Hz, 4H), 1.43 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm)143.4, 142.9, 139.3, 138.0, 130.7, 125.1, 125.0, 123.6, 116.1, 108.4, 34.4, 31.6. MS (MALDI-TOF) [m/z]: calcd for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S, 772.41; found, 772.6925. Anal. Calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S (%): C, 80.79; H, 7.30; N 3.62; S, 4.15, found: C, 80.56; H, 7.42; N 3.68; S, 4.18.

# Synthesis of 3,6-di-*tert*-butyl-9-(3-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenylsulfonyl)phenyl) -9*H*-carbazole (5a)

A procedure similar to that used for **3a** was followed but with **5b** (0.376 g, 1.0 mmol) instead of **3b**.Yield: 68.56%. M.p.:195-196 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.24-8.08 (m, 8H), 8.87-8.78 (m, 4H), 7.50-7.41 (m, 6H), 7.36-7.33 (d, J=8.7Hz, 2H), 1.47-1.46 (d, J=2.4Hz, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm)143.8, 143.5, 143.1, 143.0, 139.3, 138.1, 138.0, 137.9, 130.6, 130.6, 129.3, 126.2, 125.0, 123.8, 123.6, 123.5, 116.2, 108.8, 108.5, 34.4, 31.6, 31.5, 29.4, 26.6. MS (MALDI-TOF) [m/z]: calcd for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S, 772.41; found, 772.8536. Anal. calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>S (%): C, 80.79; H, 7.30; N 3.62; S, 4.15.found:C, 80.87; H, 7.25; N 3.63; S, 4.16.

# 3. Results and discussion

# 3.1 Synthesis and characterization

Scheme 1 and scheme 2 show the structures and synthetic routes of the synthesized **1a-5a**. Firstly, 3,6-di-*tert*-butylcarbazole was synthesized according to the literature procedure [41]. Subsequently,

bromobenzene reacted with benzenesulfonyl chloride under the catalyst of aluminum chloride to provide the intermediate **1b.** The intermediates **2b, 4b** were synthesized via brominating by *N*-Bromosuccinimide in sulfonic acid with diphenyl sulfone as the starting material. The intermediates **3b, 5b** were similarly synthesized through two steps. The diphenylsulfides were prepared with 4-bromo-thiophenol, 4-bromo-iodobenzene and 3-bromo-iodobenzene as materials via C-S coupling according to the literature procedure [42]. The resulting **3c, 5c** went through oxidization by  $H_2O_2$  to provide **3b, 5b**. Finally, Ulmann coupling reaction of bromo-substituted diphenyl sulfone with 3,6-di-*tert*-butylcarbazole led to **1a-5a** with a yield of 55.48% - 68.56%. The products were purified by the silica column method and recrystallized from n-hexane/CH<sub>2</sub>Cl<sub>2</sub>, yielding the very pure white powders. <sup>1</sup>H NMR, <sup>13</sup>C NMR, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and elemental analysis were employed to confirm the chemical structure of **1a-5a** in the experimental section.

#### **3.2 Structure Properties**

The molecular structure of **1a** was further determined by single-crystal X-ray crystallographic analysis. The single crystal of **1a** was obtained from slow evaporation of toluene solution at room temperature, and the deposition number was CCDC 973776, and the crystal data were summarized in Table 1. As shown in Fig. 1, **1a** reveals a twisted molecular structure with a dihedral angle of 49° between carbazole unit and the adjacent phenyl ring, and a dihedral angle of 106.1° between two phenyl rings. The fact that the angles for O2-S-O1 and C6-S-C7 are 120.0° and 106.1° may attribute to the hydrogen bonds between O2, O1 and C12, C5. From the data mentioned above, the non-planarity and rigidity of the molecule is established, features which are essential in preventing molecule from close packing and hence severe concentration quenching. The sulfone unit in the

structure is beneficial for the reduction of  $\pi$ -conjugation, possibly leading to high triplet energy.

#### 3.3 Thermal properties of 1a-5a

The thermal properties of **1a-5a** were investigated by thermal gravimetric analyses (TGA) under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The thermal gravimetric curves of **1a-5a** are presented in Fig. 2. The comparison of the results is shown in Table 2. The results revealed that **1a-2a** present two main decomposition processes and **3a-5a** present only one main decomposition process. The initial decomposition temperature of **1a-5a** range from 172 °C to 370 °C and the final decomposition temperature of **1a-5a** range from 443 °C to 574 °C. The number of the donor affects the Td of **1a-5a** significantly, **1a-2a** have similar lower Td values than **3a-5a**. These may attribute to more bulky structure of **3a-5a** than that of **1a-2a** [14].

#### 3.4 The UV-vis absorption spectra

Fig. 3 depicts the UV-vis absorption spectra of **1a-5a** in toluene. Three major absorption bands locate at the range of 295-298 nm, 329-333 nm and 340-345 nm in the absorption spectra, corresponding to the  $\pi$ - $\pi$ \* transitions of phenyl in 3,6-di-*tert*-butylcarbazole, diphenyl sulfone and the ICT transition. From the absorption edge of the UV-vis absorption, the optical bandgap (Eg) of **1a-5a** can be estimated to be 3.21 - 3.46 eV. The results show that the position of the donor affects the Eg value significantly. **1a** exhibits a lower Eg value than **2a**, **3a** and **5a** exhibit lower Eg values than **4a**, these may be attributed to the longer conjugation of **1a**, **3a** and **5a** than that of **2a**, **4a**. The number of the donor has a slight effect on the value of the band gap. As shown in Fig. 3, the magnitude of the band gap increased with the decrease of the number of the donor. These observations suggest that a donor-acceptor (D-A)-type structure exhibits a higher Eg value than a donor-acceptor-donor (D-A-D)-type structure. This may be attributed to the decrease of ICT leading to reduced  $\pi$ - conjugation and wide bandgap.

#### 3.5 Photoluminescence

Fig. 4 depicts the photoluminescence (PL) spectra of 1a-5a in toluene. Their photoluminescence properties are presented in Table 3. 1a-5a exhibit broad and structureless emission bands with a maximum at 404-422 nm in toluene, which can be ascribed to the ICT. As is the case with the  $\lambda_{max}$ values of **1a-5a**, their emission maxima ( $\lambda_{fl}$ ) are generally dependent on the position of the donor. Introduction of 3,6-di-tert-butylcarbazole at the 3-position of the diphenyl sulfone induces a shift of the emission maximum to longer wavelengths. The results are similar to dibenzothiophene S, S-dioxide(DBTO)-based flourophores [37]. Among them, changing the position of N-carbazole group from 3,6-substitutions to 2,7-substitutions induces a shift of the emission maximum from 424nm to 442nm. Conversely, the presence of fewer donors reduces the electron-donating ability and produces a shift of the emission maximum to shorter wavelengths. We measured the fluorescence spectra in various solvents with different polarities. In the polar solvent methanol, the emission maximum of 1a-5a red-shift to 474-479 nm. Conversely, in the nonpolar solvent hexane, the emission maximum of 1a-5a blue-shift to 369-393 nm. The Stokes shifts for 1a-5a are very large in polar solvents as compared to non-polar solvents indicating a considerable energetic stabilization of the excited state in polar solvents.

The phosphorescence spectra of **1a-5a** measured from a frozen 2-methyltetrahydrofuran matrix at 77K is shown in Fig. 5. The triplet energy of **1a-5a** was determined to the values of 2.75-3.13 eV by the energy 0-0 phosphorescent emission. **1a** has the highest triplet energy of 3.13 eV, which is in agreement with the anticipation in single-crystal X-ray crystallographic analysis.

#### **3.6 Lippert-Mataga calculation**

The solvent dependence of the fluorescence indicates that the excited state is stabilized in more polar solvents, as expected for an ICT. To obtain more information about the change in the dipole moment upon excitation, we use the Lippert-Mataga equation, Eq. (1), which express the Stokes shift as a function of the solvent polarity parameter  $\Delta f(\varepsilon, n)$  [43-44].

$$\Delta v = v_a - v_f = \left(2\Delta\mu^2 / hca^3\right) \Delta f\left(\varepsilon, n\right) + A \tag{1}$$

Where  $\Delta f(\varepsilon, n)$  is calculated from Eq. (2):

$$\Delta f(\varepsilon, n) = \left[ (\varepsilon - 1) / (2\varepsilon + 1) \right] - \left[ (n^2 - 1) / (2n^2 + 1) \right]$$
(2)

Here,  $\Delta v = v_a - v_f$  corresponds to the Stokes shift (in cm<sup>-1</sup>) between the maxima of absorption and fluorescence emission. The other terms are: *h* corresponds to the Plank's constant (6.6×10<sup>-34</sup> J s), *c* is the velocity of light in the vacuum (3.0×10<sup>8</sup> m s<sup>-1</sup>) and *a* is the solute cavity radius (m), respectively. In Eq. (2), n and  $\varepsilon$  are the refractive index and the static dielectric constant of the solvent, respectively.

Table 3 lists the  $\Delta \nu$  values for **1a-5a** in different solvents. For owing the similar structure with the reported compound based on carbazole and sulfone [36], we assumed the cavity radius of **1a-5a** to be ca. 1 nm. Fig. 6 shows the linear Lippert-Mataga plots with the slope values of 9272 cm<sup>-1</sup> -17130 cm<sup>-1</sup> for **1a-5a**. From the slope of this plot, the difference of the dipole moment between the excited state and the ground state ( $\Delta \mu$ ) were estimated to be 33 - 45 D for **1a-5a**. This large change in dipole moment upon excitation is typical for photoinduced ICT processes, reflecting the effective electronic communication between the donor 3,6-di-*tert*-butylcarbazole group and the acceptor diphenyl sulfone [36].

#### **3.7 Delayed fluorescence**

In addition, we determined the absolute fluorescence quantum yields ( $\Phi_f$ ) of **1a-5a** in toluene

solution in air and in oxygen-free (by bubbling nitrogen through the solutions for 10 minutes to exclude oxygen) by an integrating sphere system. The excitation wavelength used was 350 nm. As shown in Table 3, the  $\Phi_f$  values of **1a-5a** are 0.221-0.548 in toluene solution in air. The positions of the donor affect the  $\Phi_{\rm f}$  values significantly. Introduction of 3,6-di-*tert*-butylcarbazole at the 4-position of the diphenyl sulfone increases the  $\Phi_{\rm f}$  values as found in 1a, 3a and 5a compared to those in 2a, 4a, this may be attributed to the longer conjugation of 1a, 3a and 5a than that of 2a, 4a. The long conjugation leads to more overlap between the HOMO and LUMO levels, which will increase the radiative decay rate of the materials according to the golden rule [45]. Meanwhile, 3a, 4a and 5a exhibit higher  $\Phi_f$  values than 1a and 2a. The observation suggests that a donor-acceptor-donor (D-A-D)-type structure exhibits a higher  $\Phi_f$  value than a donor-acceptor (D-A)-type structure. For all the five compounds, the  $\Phi_{\rm f}$  values increased after nitrogen bubbling, suggesting that nitrogen bubbling suppressed the quenching of triplet states by oxygen in air and led to increased delayed fluorescence and  $\Phi_{\rm f}$  values. The larger increase in  $\Phi_{\rm f}$  values of **3a**, **4a** than those of 1a, 2a in the absence of oxygen show that (D-A-D)-type structures can emit more delayed fluorescence than the corresponding (D-A)-type structures. These findings are in line with the emitters reported by Lee [29]. The largest increase in  $\Phi_{\rm f}$  value indicates that 4a may be the best TADF emitter among 1a-5a.

Table 3 lists the prompt and delayed fluorescence lifetime of **1a-5a** in toluene. In air, these solutions have a lifetime of 4-6 ns attributing to the prompt fluorescence. After bubbling nitrogen through the solutions for 10 minutes to exclude oxygen, as shown in Fig. 7 and S1 (In the supporting information), the transient photoluminescence decay characteristics these solutions show two-component decays attributing to the prompt and delayed fluorescence, which are consistent

with the results reported by Zhang et al [27]. The delayed fluorescence of 1a-5a in toluene, which has a lifetime of 234-285  $\mu$ s, is more than four orders of magnitude longer than the prompt fluorescence, which has a lifetime of 6-30 ns. Observation that 4a shows the largest increase in the lifetime of delayed fluorescence comparing to prompt fluorescence reveals that 4a may be the most potential TADF emitters among 1a-5a.

#### 3.8 Electrochemical analysis

The electrochemical properties of **1a-5a** were studied in solution through cyclic voltammetry (CV) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard. The highest occupied molecular orbital (HOMO) energy levels of **1a-5a** were characterized (Fig. 8). During the anodic scan in  $CH_2Cl_2$  solutions, **1a-5a** exhibited similar reversible oxidation process, which can be assigned to the oxidation of electron-donating 3,6-di-*tert*-butylcarbazole moiety. No reduction waves were detected. On the basis of the onset potentials for oxidation, the HOMO energy levels of **1a-5a** were estimated to be -5.35 - -5.42 eV. The effect of the number of the donor on the HOMO energy level is not evident. The LUMO energy level of **1a-5a** estimated from the HOMO energy level and Eg were -2.21 - -1.93 eV.

#### **3.9 DFT calculations**

DFT calculations were performed to understand the physical properties of **1a-5a** at the molecular level. The results are listed in Table 4, and the HOMOs and LUMOs of **1a-5a** are shown in Fig.9. All the HOMOs of **1a-5a** are evenly delocalized over the outer 3,6-di-*tert*-butylcarbazole. The LUMOs of **1a-5a** are mainly delocalized over the central diphenyl sulfone. The theoretically calculated HOMO–LUMO gaps ( $\Delta E_{HOMO-LUMO}$ ) are higher than those obtained in the UV–vis spectroscopic measurements ( $\Delta Eg$ ) by ca. 0.5 eV, probably reflecting that the calculations are

employed under the gas-phase conditions. With respect to the effects of the conjugation in **1a-5a** on their HOMO and LUMO levels, the theoretical calculations are generally consistent with the results obtained by the absorption spectra and CV. The five compounds exhibit small variations of HOMO levels ranging from -5.37 to -5.46 eV, whereas their LUMO levels vary in a larger range from -1.48 to -1.61eV, depending on the coupling modes of electron-donating moiety carbazole and the electron-accepting moiety diphenyl sulfone.

Time dependent density functional theory (TD-DFT) calculations can also predict the  $\Delta E_{ST}$  changes of these five compounds, based on their ground state geometries when optimized by the DFT (B3LYP/6-31G\*). Using the most popular B3LYP density functional, the triplet energy of **1a-5a** were calculated to be 2.98-3.13 eV, which are in good agreement with the results based on the phosphorescence spectra of **1a-5a** measured from a frozen 2-methyltetrahydrofuran matrix at 77K except **2a**. The singlet energy of **1a-5a** was calculated to be 3.26-3.45 eV. The  $\Delta E_{ST}$  values of **1a-5a** were calculated to be 0.22-0.39 eV. In comparison with **1a** and **3a**, **2a** and **4a** show greater separation of the HOMO and LUMO orbitals. The lower overlap between the HOMO and the LUMO of **2a** and **5a** are larger than that of **2a**, **4a** also confirm that the larger overlap between the HOMO and LUMO of materials with 3,6-di-*tert*-butylcarbazole at the 4-position. The calculated results are in good agreement with the observations in the  $\Phi_f$  and lifetime. As shown in Fig. 9, the energy difference between singlet and triplet ( $\Delta E_{ST}$ ) in **1a-5a** is tuned from 0.39 eV to 0.22 eV by manipulation of the position and the number of the electron donor units.

## 4. Conclusions

In summary, we have designed and synthesized a series of

3,6-di(*tert*-butyl)-9-((phenylsulfonyl)phenyl)-9*H*-carbazoles. Their thermal and photo-physical properties have been investigated in detail by TGA, UV-vis, fluorescence spectroscopic measurements, CV and DFT calculations. The energy gap between singlet and triplet ( $\Delta E_{ST}$ ) in these compounds is tuned from 0.39 eV to 0.22 eV by manipulation of the position and the number of the electron donor units. Based on this study, we present a novel strategy for tuning the energy gap between singlet and triplet in ambipolar systems for TADF by manipulation of conjugation of the electron donor units.

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#### Figure Captions

- Scheme 1. Structure of 1a-5a.
- Scheme 2. Synthetic route of 1a-5a.
- **Table 1.** Crystal data and structure refinement for 1a.
- **Table 2.** Values of the initial  $(T_{di})$ , final decomposition temperatures  $(T_{df})$ ,  $T_d$  (corresponding to a weight-loss of 5%) of **1a-5a** from the TGA.
- **Table 3.** Photoluminescence properties of 1a-5a.
- Table 4. Cyclic voltammetry, photoluminescence properties and theoretically calculated energy levels of 1a-5a.
- Fig. 1. ORTEP diagram of 1a.
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- Fig. 3. Normalized UV-vis absorption spectra of 1a-5a.
- Fig. 4. Normalized photoluminescence spectra of 1a-5a.
- Fig. 5. The phosphorescence spectra of **1a-5a** measured from a frozen 2-methyltetrahydrofuran matrix at 77K.
- Fig. 6. Lippert-Mataga plots of 1a-5a.
- **Fig. 7.** Emission decay of **1a-5a** in the absence of oxygen (by bubbling nitrogen through the solution for 10 minutes to exclude oxygen) in toluene at 300 K.
- **Fig. 8.** Oxidation part of the CV curves of **1a-5a** in  $CH_2Cl_2$  solutions (10<sup>-3</sup>M).
- **Fig. 9.** Optimized geometries and calculated HOMO and LUMO density maps for **1a-5a** according to DFT calculations at B3LYP/6-31\* level.
- S1. Emission decay curves and fitting curves of 1a-5a in the absence of oxygen (by bubbling

nitrogen through the solution for 10 minutes to exclude oxygen) in toluene at 300 K. The value of Adj. R-Square (>0.967) is used to ensure the quality of the fit.

ubic 1	Empirical formula	C <sub>32</sub> H <sub>33</sub> NO <sub>2</sub> S
	CCDC No.	973776
	Formula weight	495.65
	Temperature	293(2)
	Wavelength	0.71073 Å
	Crystal system, space group	monoclinic
	Unit cell dimensions	$a = 9.945(2)$ Å $\alpha = 90.00^{\circ}$
		$b = 11.848(2) \text{ Å} \qquad \beta = 90.27(3)^{\circ}$
		$c = 11.506(2) \text{ Å}$ $\gamma = 90.00^{\circ}$
	Volume	1355.7(5) Å <sup>3</sup>
	Z, Calculated density	2, 1.214 Mg/m <sup>3</sup>
	Absorption coefficient	0.148 mm <sup>-1</sup>
	<i>F</i> (000)	528
	Crystal size	$0.10 \times 0.20 \times 0.30 \text{ mm}$
	Theta range for data collection	1.77 to 25.39 deg.
	Limiting indices	0<=h<=12, -14<=k<=14, -13<=l<=13
	Reflections collected / unique	$4971 / 3667 [R_{\rm int} = 0.0631]$
	Max. and min. transmission	0.9853 and 0.9569
	Refinement method	Full-matrix least-squares on $F^2$
	Data / restraints / parameters	4971 / 1 / 325
	Final R indices [I>2sigma(I)]	$R_1 = 0.0588, wR_2 = 0.1435$
	Largest diff. peak and hole	0.251 and -0.177 e·Å <sup>-3</sup>

**Table 1**Crystal data and structure refinement for 1a.

	Compd.	T <sub>di</sub> (°C)	$T_{df}(^{o}C)$	$T_d (^{o}C)$					
	1a	220	452	297					
	2a	170	443	332					
	<b>3</b> a	370	549	427					
	<b>4</b> a	369	560	421					
	5a	342	574	371					

**Table 2** Values of the initial  $(T_{di})$ , final decomposition temperatures  $(T_{df})$ ,  $T_d$  (corresponding to aweight-loss of 5%) of **1a-5a** from the TGA

Table 3	Photoluminescence	properties	of 1a-5a
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	M(c, r)		1a			2a			<b>3</b> a	$\mathbf{O}$		4a			5a	
	ц ( <i>ъ</i> , п)	UV	PL	$\Delta \nu$	UV	PL	$\Delta \nu$	UV	PL	$\Delta v$	UV	PL	$\Delta v$	UV	PL	$\Delta \nu$
hexane	0	343	377	2629	341	389	3619	344	369	1969	341	393	3880	343	379	2769
toluene	0.013	344	406	4439	342	414	5085	345	404	4355	342	422	5543	344	410	4679
DCM	0.217	344	445	6598	342	451	7067	345	449	6714	342	458	7406	344	452	6946
DMF	0.274	344	453	6995	343	462	7509	345	460	7246	342	470	7963	345	462	7340
MeOH	0.307	345	474	7888	344	479	8193	346	475	7849	343	484	8493	345	477	8021
Slope			17130			14899			11076			9272			10963	
$\Delta\mu$ (d)			45			42			36			33			36	
Phos (nm) <sup>a</sup>			396			451			403			405			416	
Triplet(eV)			3.13	$\mathcal{I}$		2.75			3.08			3.06			2.98	
Eg(nm)			375			358			386			364			379	
Eg(eV)		X	3.31			3.46			3.21			3.41			3.27	
$\Phi_{\mathrm{f}}^{}b}$			0.405			0.221			0.536			0.362			0.548	
$\Phi_{\mathrm{f}}{}^{c}$			0.587			0.507			0.690			0.656			0.777	
$\Delta \Phi_{ m f}$			0.182			0.286			0.154			0.294			0.229	
$\tau_p(ns)^{b}$			5.57			4.68			5.31			5.59			5.20	
$\tau_p(ns)^{c}$			6.38			16.6			6.34			22.35			8.36	

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$\tau_{d}$ (µs) <sup>c</sup>	234	258	250	285	257				

<sup>a</sup> The phosphorescence spectra of **1a-5a** are measured from a frozen 2-methyltetrahydrofuran matrix at 77K.

 ${}^{b}\Phi_{f}$ , and  $\tau_{p}$  of **1a-5a** are determined in toluene.

<sup>c</sup> In the absence of oxygen (by bubbling nitrogen through the solution for 10 minutes to exclude oxygen).

**Table 4** Cyclic voltammetry, photoluminescence properties and theoretically calculated energylevels of 1a-5a.

	<b>1</b> a	2a	3a	<b>4</b> a	5a
LUMO(eV) <sup>a</sup>	-1.49	-1.48	-1.59	-1.61	-1.61
LUMO(eV)	-2.07	-1.93	-2.10	-2.21	-2.18
HOMO(eV) <sup>a</sup>	-5.47	-5.37	-5.41	-5.38	-5.42
HOMO(eV)	-5.42	-5.36	-5.35	-5.36	-5.41
Eg(eV) <sup>a</sup>	3.97	3.89	3.82	3.77	3.80
Eg(eV)	3.31	3.46	3.21	3.41	3.27
Singlet(eV) <sup>a</sup>	3.45	3.36	3.31	3.26	3.30
Triplet(eV) <sup>a</sup>	3.06	3.12	2.98	3.04	2.99
Triplet(eV)	3.13	2.75	3.08	3.06	2.98
$\Delta E_{ST} (eV)^{a}$	0.39	0.24	0.33	0.22	0.31

<sup>a</sup> Theoretically calculated energy levels of **1a-5a**.



**Fig. 1.** ORTEP diagram of **1a**.



Fig. 2. TGA curves of 1a-5a.



**Fig. 3.** UV absorption spectra of **1a-5a** in toluene. $(10^{-4} \text{ mol L}^{-1})$ 



Fig. 4. Fluorescence spectra of 1a-5a in toluene.



**Fig. 5.** The phosphorescence spectra of **1a-5a** measured from a frozen 2-methyltetrahydrofuran matrix at 77K.



Fig. 6. Lippert-Mataga plots of 1a-5a.



**Fig. 7.** Emission decay of **1a-5a** in the absence of oxygen (by bubbling nitrogen through the solution for 10 minutes to exclude oxygen) in toluene at 300 K.



**Fig. 8.** Oxidation part of the curves of **1a-5a** in  $CH_2Cl_2$  solutions (10<sup>-3</sup> M).



Fig. 9. Optimized geometries and calculated HOMO and LUMO density maps for 1a-5a.

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Scheme 2. Synthetic routes for 1a-5a.

A series of materials for thermally activated delayed fluorescence is synthesized.

The structure-property relationships are studied.

The energy gap between singlet and triplet is tuned from 0.39 eV to 0.22 eV.



**Figure S1.** Emission decay curves and fitting curves of **1a-5a** in the absence of oxygen (by bubbling nitrogen through the solution for 10 minutes to exclude oxygen) in toluene at 300 K. The value of Adj. R-Square (>0.967) is used to ensure the quality of the fit.