

## Supporting Information

### Enhancement of radiative constants by introducing intramolecular hydrogen bonding into thermally activated delayed fluorescent (TADF) materials

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### General Information

All the organic materials are purchased from commercial sources and used without further purification.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> by a Switzerland Bruker DR × 600 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Netzsch TG 209F3 and DSC Q2000 thermal analyzers under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Absorption and photoluminescence (PL) emission spectra of the target compound were measured using a Lambda Bio 40 and a HORIBA FluoroMax-4 spectrophotometer, respectively. PL

quantum yields and transient PL decay are measured using Edinburgh Instruments FLS980 spectrometer. The electrochemical properties of three materials were obtained by cyclic voltammetry (CV) measurements using a CHI 660E voltametric analyzer. The electrolyte was Tetra-n-butylammonium perchlorate (TBAP) in anhydrous dichloromethane (0.1 M). A platinum wire was used as the working electrode. The platinum electrode was the counter electrode, the calomel electrode was the reference electrode, and ferrocene-ferrocene ( $\text{Fc}^+/\text{Fc}$ ) was the internal standard. Single-crystal X-ray structure analysis was obtained using Bruker APEX-II CCD Venture X-ray single crystal diffractometer.

### **DFT calculation**

The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP functional at the basis set level of 6-31G(d), and the natural transition orbitals (NTOs) analysis has been performed at the B3LYP/6-31G(d) level with time-dependent DFT (TD-DFT) methods. The above two calculations were performed using Gaussian09 software package. The weak interactions present within the molecules were analyzed using a multifunctional wavefunction analyzer (Multiwfn 3.8) and visualized with VMD program (1.9.3). The SOCMEs of three materials were calculated with the ORCA program.

### **Synthetic of compounds**

**Synthesis of (4-fluorophenyl) (5-fluoropyridin-2-yl) methanone (1).** A mixture of compound 5-fluoropicolinic acid (705.5 mg, 5 mmol), N, O-Dimethyl hydroxylamine hydrochloride (585.25 mg, 6 mmol), triethylamine (607.1mg, 6 mmol), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI) (2300.4 mg, 12 mmol) and anhydrous

dichloromethane (20 mL) was stirred at room temperature under nitrogen atmosphere for 12 h. The mixture was poured into 50 mL water,

and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic solution was evaporated under vacuo to afford intermediate products. Then, the intermediate products were dissolved in 10 ml dry tetrahydrofuran (THF) at 0°C and 4-Fluorophenylmagnesium bromide (6 mL, 6 mmol, 1 M in THF) was added dropwise. The mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by saturated ammonium chloride solution and extracted with ethyl acetate for three times. The combined organic phases were washed three times with water and then dried with anhydrous MgSO<sub>4</sub>. The solvent was removed and the resultant crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane mixture (5:1, v/v) as the eluent to afford compound **1** as a white solid. (yield 68%). <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.54 (d, J = 2.8 Hz, 1H), 8.24 – 8.12 (m, 3H), 7.60 (ddd, J = 8.7, 8.1, 2.8 Hz, 1H), 7.21 – 7.12 (m, 2H).

**Synthesis of (4-fluorophenyl) (6-fluoropyridin-3-yl) methanone (2).** The synthetic process of **2** was similar to that for **1** as white powder with a yield of 74%. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.60 (d, J = 2.3 Hz, 1H), 8.28 – 8.20 (m, 1H), 7.86 – 7.79 (m, 2H), 7.23 – 7.15 (m, 2H), 7.07 (dd, J = 8.5, 2.8 Hz, 1H).

**Synthesis of bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl) phenyl) methanone (BTC).** 3,6-Di-tert-butylcarbazole (614.72 mg, 2.2 mmol) and 15 mL dry dimethylformamide (DMF) were added to a 50 ml three-necked flask and t-BuOK (235.64 mg, 2.1 mmol) was added under nitrogen atmosphere and the mixture was stirred at room temperature

for 30 min. bis(4-fluorophenyl) methanone (229.11 mg, 1.05 mmol) was dissolved in 5 mL dry dimethylformamide (DMF) and added drop by drop to the reaction flask. After the addition was completed, the reaction temperature was raised to 110° C and stirred for 24 h. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate for three times. The combined organic solution were washed with brine three times. After dried over anhydrous MgSO<sub>4</sub>, the solvent was removed under reduced pressure and the residue was purified with column chromatography on neutral alumina using petroleum ether/Dichloromethane mixture (5:1, v/v) as the eluent to afford the product as white powder in 52% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.16 (s, 8H), 7.79 (d, J = 8.4 Hz, 4H), 7.51 (s, 8H), 1.48 (s, 36H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 143.70, 142.38, 138.58, 135.36, 131.85, 125.86, 123.94, 123.91, 116.45, 109.32, 34.80, 31.99. found:736.42.

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

**-9-yl) pyridin-2-yl) methanone (B2-TC).** The synthetic process of **B2-TC** was similar to that for **BTC** as yellowish green powder with a yield of 62%. <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 9.10 (d, J = 2.3 Hz, 1H), 8.48 (d, J = 8.4 Hz, 2H), 8.42 (d, J = 8.3 Hz, 1H), 8.18 (ddd, J = 22.9, 9.3, 2.0 Hz, 5H), 7.79 (d, J = 8.5 Hz, 2H), 7.62 – 7.41 (m, 8H), 1.49 (s, 36H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 145.77, 144.44, 143.65, 138.54, 138.29, 133.02, 126.06, 125.57, 124.31, 124.22, 123.95, 123.88, 116.69, 116.39, 109.48, 108.94, 34.85, 34.80, 31.99, 31.96. HRMS(C<sub>52</sub>H<sub>55</sub>N<sub>3</sub>O):*m/z* [M+H<sup>+</sup>] calcd 738.4417; found: 738.4428.

## Synthesis of (4-(3,6-di-tert-butyl-9H-carbazol-9-yl) phenyl) (6-(3,6-di-tert-butyl-9H-carbazol-

9-yl) pyridin-3-yl)methanone (**B3-TC**). The synthetic process of **B3-TC** was similar to that for **BTC** as yellowish green powder with a yield of 58%. <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 9.20 (d, J = 2.3 Hz, 1H), 8.45 (dd, J = 8.4, 2.1 Hz, 1H), 8.21 – 8.08 (m, 6H), 8.02 (d, J = 8.7 Hz, 2H), 7.83 (dd, J = 31.0, 8.3 Hz, 3H), 7.57 – 7.46 (m, 6H), 1.48 (d, J = 3.0 Hz, 36H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 155.12, 151.51, 145.07, 143.81, 139.75, 138.50, 131.74, 129.11, 125.97, 125.21, 124.25, 124.00, 123.95, 116.48, 116.29, 111.70, 109.31, 34.83, 34.81, 31.99, 31.89. HRMS(C<sub>52</sub>H<sub>55</sub>N<sub>3</sub>O):*m/z* [M+H<sup>+</sup>] calcd 738.4417; found: 738.4424.

## OLED fabrication and characterization

OLEDs are fabricated on indium tin oxide (ITO) glass substrates by thermal vacuum deposition. Therefore, before loading into the deposition chamber, we cleaned the glass substrate using detergent, deionized water, acetone and isopropyl alcohol in that order. After cleaning, they were placed in an oven at 120 °C for 4 hours and treated with UV ozone for 20 minutes. Devices were fabricated by evaporating organic layers at a rate of 0.1- 0.3 nm s<sup>-1</sup> onto the ITO substrate sequentially at a pressure below 1 × 10<sup>-6</sup> mbar. The effective emitting area of the devices is 9 mm<sup>2</sup>, determined by the overlap between anode and cathode.

The luminance–voltage–current density characteristics and Electroluminescence (EL) spectra were obtained via a computer-controlled Keithley 2400 source meter integrated with a BM-70A luminometer and a PR-655 spectrophotometer. The external

quantum efficiency (EQE) was estimated using normalized EL spectra and the current efficiency of the device. All characterizations were performed at room temperature and ambient conditions without any encapsulation.

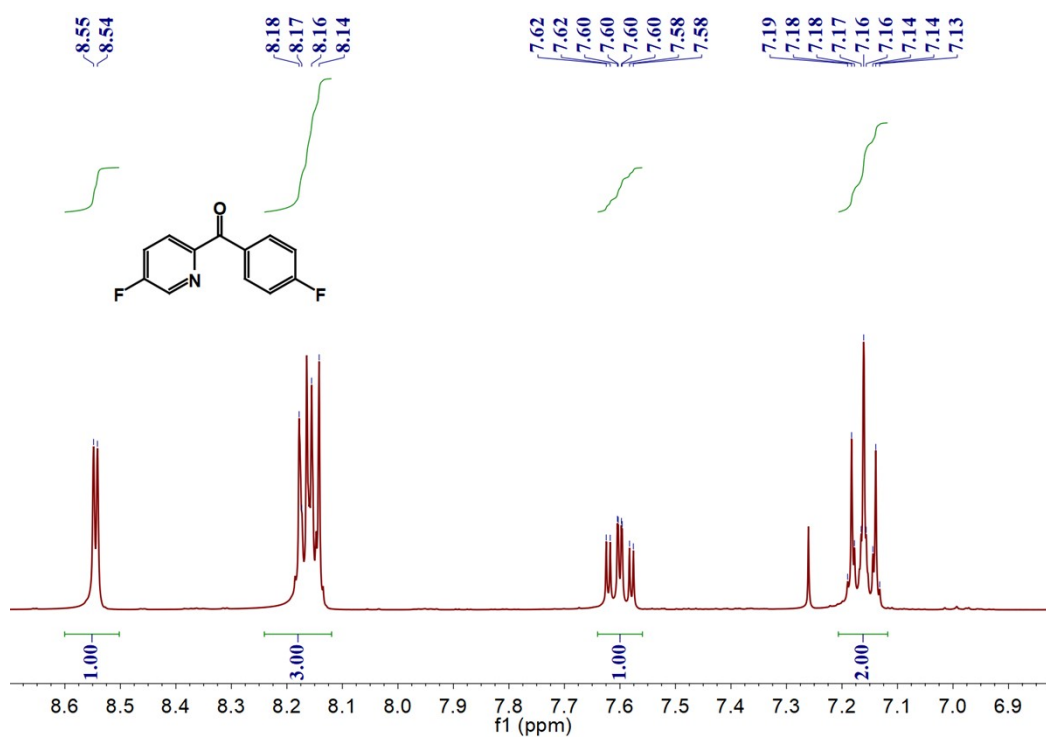


Fig. S2. <sup>1</sup>H NMR spectrum of intermediate 1 in CDCl<sub>3</sub>

Table S2. Summary of singlet and trilinear excited state levels.

Compound	S <sub>1</sub> /eV	T <sub>1</sub> /eV	T <sub>2</sub> /eV	T <sub>3</sub> /eV	T <sub>4</sub> /eV	T <sub>5</sub> /eV
BTC	2.201	2.153	2.543	2.721	2.733	2.933
B2-TC	1.840	1.804	2.102	2.488	2.493	2.662
B3-TC	2.153	2.088	2.360	2.487	2.601	2.758

Table S1. Summary of spin orbit coupling matrix constants of S<sub>1</sub> and T<sub>1</sub>-T<sub>5</sub>

Compound	$\langle S_1   H_{\text{soc}}   T_1 \rangle$	$\langle S_1   H_{\text{soc}}   T_2 \rangle$	$\langle S_1   H_{\text{soc}}   T_3 \rangle$	$\langle S_1   H_{\text{soc}}   T_4 \rangle$	$\langle S_1   H_{\text{soc}}   T_5 \rangle$
BTC	0.632	0.031	2.407	0.278	0.02
B2-TC	0.405	0.253	3.612	0.088	0.049
B3-TC	0.691	0.196	2.093	0.642	0.198

