Electronic Supplementary Information for

The role of fluorine substitution on the π -bridge in constructing

effective thermally activated delayed fluorescence molecules

Yun Li,^a Jiao-Jiao Liang,^a Hong-Cheng Li,^a Lin-Song Cui,^c Man-Keung Fung,^a Seth R. Marder,^{b*} Stephen Barlow,^b Chihaya Adachi,^c Zuo-Quan Jiang,^{a*} and Liang-Sheng Liao^a

^a Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Joint International Research Laboratory of Carbon-Based

Functional Materials and Devices, Soochow University, Suzhou 215123, P. R. China.

^{b.} School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

^{c.} Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395 Japan.

1. General methods	2
2. Fabrication and measurement of OLED devices	3
3. Synthesis and characterization	3
5. Supplementary data	6
6. The materials used in the devices	13
7. References	13

1. General methods

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 600 spectrometer at room temperature. Time-offlight (TOF) MALDI mass spectra were acquired on a Bruker Auto flex II/Compass 1.0 from Soochow University, Department of Materials Science and Engineering. Elemental analyses (C, H and N) were carried out with a VARIO EL III elemental analyzer. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra, including phosphorescence, spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The prompt and delayed PL spectra of the samples were measured under a vacuum using a streak camera system (Hamamatsu Photonics, C4334) equipped with a cryostat (Iwatani, GASESCRT-006-2000, Japan). A nitrogen gas laser (Lasertechnik Berlin, MNL200) with an excitation wavelength of 337 nm was used. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C min⁻¹ under nitrogen. The glass transition temperatures (T_{g}) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min⁻¹ under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature (T_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferroceniumferrocene as the internal standard. Deaerated dichloromethane was used as solvent for oxidation and reduction scan with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at scan rate of 0.1 V s⁻¹. The ground state geometry optimization has been performed with DFT with the B3LYP hybrid functional and def2svp basis set using Gaussian 09 and the excited state calculations were conducted using TD-DFT/PBE1PBE/def2svp. The Multiwfn-3.3.9-bin-Win software is used for the orbital composition analysis.¹

2. Fabrication and measurement of OLED devices

The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, the ITO conductive layer has a thickness of ca. 100 nm and a sheet resistance of ca. 30 Ω per square. The substrate was cleaned with ethanol, acetone and deionized water, and then dried in an oven, finally exposed to UV ozone for 15 min. All of the organic materials and metal layers were deposited under a vacuum of ca. 10⁻⁶ Torr. Three identical OLED devices were formed on each of the substrate and the emission area of 0.09 cm² for each device. The electroluminescence (EL) performances of the devices were measured with a PHOTO RESEARCH SpectraScan PR 655 PHOTOMETER and a KEITHLEY 2400 SourceMeter constant current source at room temperature.

3. Synthesis and characterization

3.1 Synthesis of TCTZ

The detailed synthetic route of compound TCTZ is described as follows; although this is a known compound ² we modified the synthetic methods. Chemicals and solvents were used as purchased from commercial suppliers without further purification.

2-(4-fluorophenyl)-4, 6-diphenyl-1, 3, 5-triazine



A mixture of (4-fluorophenyl) boronic acid (1.89 g, 13.5 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (3.00 g, 11.3 mmol), sodium carbonate (6.00 g, 56.3 mmol) and tetrakis(triphenylphosphine)palladium (0.51 g, 0.56 mmol) in 150 mL toluene, 21 mL ethanol and 30 mL water under argon was refluxed for 12 h. After cooling to room temperature, the resulting product was diluted with CH_2Cl_2 and washed with water. The combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using 1:4 CH_2Cl_2 / petroleum as eluent to afford a white solid (3.30 g, 90%)³. MS (m/z): 327.26 [M]⁺.

9'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9'H-9,3':6',9"-tercarbazole (TCTZ)



Under argon atmosphere 9'*H*-9,3':6',9"-tercarbazole (0.89 g, 1.80 mmol), 2- (4-fluorophenyl) -4,6-diphenyl -1,3,5triazine (0.71 g, 2.15 mmol), and potassium carbonate (1.30 g, 75 mmol) were suspended in DMSO (40 mL) and

stirred for 12 h at 150 °C. After the reaction cooling to room temperature, the solution was poured into the water and then filtered and washed with CH_2CI_2 . Removal of the CH_2CI_2 of the organic phase under reduced pressure gave the crude product, which was purified by column chromatography using petroleum 1:4 CH_2CI_2 / petroleum to afford the pure product as a white solid (1.12 g, 80%). MS (m/z): 804.62 [M]⁺. Anal. calcd for $C_{57}H_{36}N_6(\%)$:C 85.05, H 4.51, N 10.44; found: C 85.01, H 4.57, N 10.39.

3.2 Synthesis of TCTZ-F





A mixture of (3,4-difluorophenyl) boronic acid (2.13 g, 13.50 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (3.00 g, 11.25 mmol), sodium carbonate (6.00 g, 56.25 mmol) and tetrakis (triphenylphosphine) palladium (0.51 g, 0.56 mmol) in 150 mL toluene, 21 mL ethanol and 30 mL water under argon was refluxed for 12 h. After cooling to room temperature, the resulting product was diluted with CH_2CI_2 and washed with water. The combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using 1:4 CH_2CI_2 / petroleum ether as eluent to afford a white solid (3.24 g, 88%). ¹H NMR (600 MHz, CDCI₃) δ 8.74 (s, 4H), 8.57 (s, 2H), 7.60 (d, *J* = 6 Hz, 6H), 7.35 (d, *J* = 6 Hz, 1H). ¹³C NMR (150 MHz, CDCI₃) δ 172.07, 170.05, 153.70 ($^{1}J_{CF}$ = 250.96 Hz), 150.92 ($^{1}J_{CF}$ = 248.55 Hz), 146.09, 136.14, 133.71, 133.04, 129.13 ($^{2}J_{CF}$ = 42.58), 125.88, 118.311 ($^{2}J_{CF}$ = 18.12 Hz), 117.81. MS (m/z): 346.03 [M] ⁺. Anal. calcd for $C_{21}H_{13}F_2N_3$ (%):C 73.04, H 3.79, N 12.17; found: C 73.00, H 3.83, N 12.20.





Under argon atmosphere 9'*H*-9,3':6',9''-tercarbazole (0.67 g, 1.35 mmol), 2-(3,4-difluorophenyl)-4,6-diphenyl - 1,3,5- triazine (0.60 g, 1.62 mmol), and potassium carbonate (1.30 g, 10.75 mmol) were suspended in DMSO (40 mL) and stirred for 12 h at 150 °C. After the reaction mixture was cooled to room temperature, it was filtered and washed with CH₂Cl₂. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography using petroleum 1:4 CH₂Cl₂ / petroleum ether to afford the pure product as a white solid (0.78 g, 78%). ¹H NMR (600 MHz, CDCl₃) δ 8.95 – 8.89 (m, 2H), 8.85 (d, *J* = 7.2 Hz, 4H), 8.32 (d, *J* = 1.8 Hz, 2H), 8.18 (d, *J* = 7.8 Hz, 4H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.68 (m, 4H), 7.63 (m, 6H), 7.43 (m, 8H), 7.30 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 172.37, 170.16, 158.46 (¹*J*_{CF} = 253.38 Hz) 142.00, 140.52, 138.92, 136.09, 133.24, 131.31, 129.80, 129.24 (²*J*_{CF} = 42.129 Hz) 126.82, 128.49, 128.40, 126.22, 124.81, 126.16, 123.50, 120.60, 120.11, 120.06, 118.34 (²*J*_{CF} = 21.59 Hz), 111.90, 109.99. MS (m/z): 822.63 [M] ⁺. Anal. calcd for C₅₇H₃₅FN₆(%):C 83.19, H 4.29, N 10.21; found: C 83.09, H 4.34, N 10.18.

3.3 Synthesis of TCTZ-2F



A mixture of (3,4,5-trifluorophenyl) boronic acid (4.28 g, 24.32 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (5.00 g, 18.7 mmol), sodium carbonate (9.00 g, 84.9 mmol) and tetrakis(triphenylphosphine) palladium (0.51 g, 0.56 mmol) in 150 mL toluene, 21 mL ethanol and 30 mL water under argon was refluxed for 12 h. After cooling to room temperature, the resulting product was diluted with chloroform and washed with water. The combined organic extracts were dried over Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using 1:4 CH₂Cl₂ / petroleum ether as eluent to afford a white solid (5.12 g, 77%). ¹H NMR (600 MHz, CDCl₃) δ 8.74 (t, *J* = 6 Hz, 4H), 8.43 (t, *J* = 6 Hz, 2H), 7.64 (m, 2H), 7.59 (m, 4H).¹³C NMR (150 MHz, CDCl₃) δ 171.92, 168.91, 151.45 ($^{1}J_{CF}$ = 250.36), 151.38 ($^{1}J_{CF}$ = 250.51), 143.48, 141.77, 135.57, 132.91, 128.99, 113.10 ($^{2}J_{CF}$ = 18.42). MS (m/z): 363.02 [M] ⁺. Anal. calcd for C₂₁H₁₂F₃N₃ (%):C 69.42, H 3.33, N 11.57; found: C 69.38, H 3.31, N 11.60.

9'-(4-(4, 6-Diphenyl-1, 3, 5-triazin-2-yl)-2,6-difluorophenyl)-9'H-9,3':6',9''-tercarbazole (TCTZ-2F)



Under argon atmosphere 9'H-9,3':6',9''-tercarbazole (0.67 g, 1.35 mmol), 2,4-diphenyl-6- (3,4,5-trifluorophenyl) - 1,3,5-triazine (0.60 g, 1.62 mmol), potassium carbonate (1.30 g, 10.75 mmol), and was scattered in DMSO (40 mL) and stirred for 12 hours at 150 °C. After the reaction cooling to room temperature, filtered and washed with CH₂Cl₂. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum 1: 4 CH₂Cl₂/ petroleum to afford the pure product as a white solid (0.78 g, 78%). ¹H NMR (600 MHz, CDCl₃) δ 8.83 (t, *J* = 6.0, 4H), 8.74 (d, *J* = 6.0 Hz, 2H), 8.32 (d, *J* = 1.8 Hz, 2H), 8.17 (d, *J* = 6.0 Hz, 4H), 7.69 (m, 4H), 7.64 (m, 4H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.44 (m, 8H), 7.30 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 172.55, 169.35, 159.59 (¹*J*_{CF} = 255.49), 141.99, 140.19, 139.40, 135.85, 133.43, 131.56, 129.32, 129.29 (²*J*_{CF} = 39.86) 126.90, 126.23, 124.98, 123.50, 120.59, 120.15, 120.07,117.40,113.51 (²*J*_{CF} = 24.37) 111.89, 110.02. MS (m/z): 840.63 [M]⁺. Anal. calcd for C₅₇H₃₄F₂N₆ (%):C 81.41, H 4.08, N 9.99; found: C 81.43, H 4.11, N 9.97.

Table S1. Excited state energies from TDDFT calculation (eV).

	Compound	$S_0 - S_1^{a}$	$S_0-S_1^{b}$	S_0-T_1 a)	S_0-T_1 b)	$\Delta E_{\rm ST}$ ^{a)}	$\Delta E_{\rm ST}$ ^{b)}
5.	TCTZ-F	2.5412	2.5417	2.4592	2.4667	0.0821	0.0751
	TCTZ-2F	2.4362	2.4298	2.3812	2.3748	0.0550	0.0550

^{a)} Calculation constrained at the torsion angle of 53.23° the same as TCTZ. ^{b)} Calculation

in adiabatic without constrained factor.

Supplementary data



Fig. S1 The ground state geometries and HOMO, LUMO contour maps and percentage of charge transfer (CT)

for S_1 states of TCTZ, TCTZ-F and TCTZ-2F.



Fig. S2 The HONTO and LUNTO distributions of charge transfer (CT) for S₁ and T₁ states and the contributions of the NTO pairs for S₀->S₁ and S₀->T₁ of TCTZ, TCTZ-F, TCTZ-2F.



Fig. S3 The hole and electron distribution for S_1 and T_1 of TCTZ, TCTZ-F and TCTZ-2F; blue and green areas represent hole and electron respectively.



Fig. S4 Cyclic voltammograms of TCTZ, TCTZ-F and TCTZ-2F in $CH_2Cl_2 / 0.1 \text{ M} [(n-Bu_4N)^+(PF_6)^-]$



Fig. S5 TGA and DSC (inset) curves of TCTZ.



Fig. S6 TGA and DSC (inset) curves of TCTZ-F.



Fig. S7 TGA and DSC (inset) curves of TCTZ-2F.



Fig. S8. Fluorescence and phosphorescence spectra of guests in toluene. Red and black lines represent fluorescence spectra at RT and phosphorescence spectra at 77 K, respectively. The supporting lines to determine S_1 and the lowest excited triplet state (T_1) energy, respectively.



Fig. S9 Fluorescence spectra of TCTZ in different solvents (10⁻⁵ M).



Fig. S10 Fluorescence spectra of TCTZ-F in different solvents (10⁻⁵ M).



Fig. S11 Fluorescence spectra of TCTZ-2F in different solvents (10⁻⁵ M).



Fig. S12 Fluorescence spectra at 77K of TCTZ, TCTZ-F and TCTZ-2F, in film.



Fig. S13 600 MHz ¹H NMR spectrum of compound TCTZ-F measured in CDCl_{3.}



Fig. S14 150 MHz $^{\rm 13}{\rm C}$ NMR spectrum of compound TCTZ-F measured in CDCl_3.



Fig. S15 600 MHz ^1H NMR spectrum of compound TCTZ-2F measured in CDCl_3.



Fig. S16 150 MHz ¹³C NMR spectrum of compound TCTZ-2F measured in CDCl_{3.}



Fig. S17 MALDI-TOF mass spectrum of TCTZ.



Fig. S18 MALDI-TOF mass spectrum of TCTZ-F.



Fig. S19 MALDI-TOF mass spectrum of TCTZ-2F.

6. Materials used in OLEDs



3TPYMB

HAT-CN

ТАРС



7. References

- Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S.-Y. Lee, H. Nomura, N. Nakamura, M. Yasumatsu, H. Nakanotani, Q. Zhang, K. Shizu, H. Miyazaki and C. Adachi, *Nat. Mater.*, 2015, 14, 330.
- 3 L.-S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani and C. Adachi, Angew. Chem. Int. Ed., 2017, 56, 1571.