## **Supporting Information**

Ester Substituted Thiophene-Fused Benzothiadiazole as a Strong Electron-Acceptor to Build D-A Red-emitters for Highly Efficient Solution-processed OLEDs

Xiaoxiao Wang, Cheng Zhong\*, Guohua Xie\*, Xingguo Chen\*

Hubei Key Laboratory on Organic and Polymeric Opto-electronic Materials, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

E-mail address: xgchen@whu.edu.cn, guohua.xie@whu.edu.cn, zhongcheng@whu.edu.cn

### **1. Experimental Section**

#### **General Methods**

All raw materials, reagents and solvents were purchased commercial sources and were used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker Advanced II (400 MHz) spectrometers, the tests used tetramethylsilane (TMS) as internal standard and CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub> as solvents. High-resolution mass spectra (HRMS) were measured on a LCQ-Orbitrap Elite mass spectrometer (Thermo-Fisher Scientific, Waltham, MA, USA). Thermogravimetric analysis (TGA) was undertaken with a NETZSCHSTA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min<sup>-1</sup> from 25 to 600 °C. Differential scanning calorimetry (DSC) was measured on a NETZSCH (DSC-204) unit from 30 °C to 300 °C at a heating rate of 10 K min<sup>-1</sup> under nitrogen atmosphere. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and Tetrahydrofuran (THF) at room temperature with a CHI voltammetric analyser. Tetrabutylammonium

hexafluorophosphate (TBAPF<sub>6</sub>) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene ( $Fc^+/Fc$ ) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s<sup>-1</sup>. The resulting HOMO/LUMO values are calculated according to the equation (unit: eV):

$$E_{\rm HOMO} = -(E_{ox} \text{ vs. Fc/Fc}^+ + 4.8)$$

$$E_{\text{LUMO}} = -(E_{\text{red}} \text{ vs. Fc/Fc}^+ + 4.8)$$

#### **Photophysical Measurement**

UV-Vis spectra were obtained using a Shimadzu UV-2700 spectrophotometer with quartz cells (1 cm path length). Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The PL lifetimes was measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UVLASTER(LASTER377) as the excitation source. Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics) and all the samples were excited at 330 nm

#### Single crystal X-ray diffraction

Data collection was performed using a Bruker SMART APEXDUO diffractometer equipped with a CCD detector (graphitemonochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$ Å) at 100 K and300 K. The software package SAINT PLUS19 was used for data set reduction and integration. The structure was solved by direct methods and refined using the SHELXTL97 software package.

#### **Theoretical Calculation Method**

All optimizations were done at PBE0/def2-SVP level with Grimme's D3BJ<sup>[1]</sup> empirical dispersion correction. Then the vertical excited states are calculated at same level with Gaussian09 program. The spin orbital coupling constants were calculated by pySOC program.<sup>[2]</sup> The electron-hole analyses of excited stated were performed using

#### Multiwfn program.<sup>[3]</sup>

#### Lippert-Mataga model

The influence of solvent environment on the optical property of the compounds has been investigated using the Lippert-Mataga equation (1):

$$hc(v_a - v_f) = hc(v_a^0 - v_{f_0}) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\varepsilon, n)$$
(1)

*f* is the orientational polarizability of solvents,  $\mu_e$  is the dipole moment of excited state,  $\mu_g$  is the dipole moment of ground state; a is the solvent cavity (Onsager) radius, this value can be calculated using Avogadro's constant (N), molecular molar mass (M) and density d=1.0 g/cm3 using formula (2):  $\varepsilon$  and *n* are the solvent dielectric and the solvent refractive index, Therefore, the formula for  $f(\varepsilon, n)$  and *a* can be expressed as:

$$f(\varepsilon,n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, a = (3M / 4n\pi d)^{\frac{1}{3}}$$
(2)

#### 2. Synthesis Characterization

### Synthesis of ethyl 4-bromothieno[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole-6carboxylate (M2)

M1(1.05 g, 3.97 mmol) was dissolved in CHCl<sub>3</sub> and Br<sub>2</sub> (1.46 g, 4.11mmol) was added at 0 °C, then the reaction mixture was stirred at 0 °C for 4 h. After the reaction, the mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> for several times. The organic phase was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and solvent evaporation, the crude product was purified by column chromatography over silica gel with petroleum / CH<sub>2</sub>Cl<sub>2</sub> as the eluent to give a yellow solid (1.01 g, 74 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.41 (s, 1H), 8.20 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 161.66, 152.72, 151.37, 143.30, 141.53, 139.29, 129.43, 113.10, 109.79, 62.43, 14.30.



Synthesis of ethyl 4,8-dibromothieno[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole-6-carboxylate (M3)

M1(1.06 g, 4.01 mmol) was dissolved in CHCl<sub>3</sub> and Br<sub>2</sub> (1.46 g, 9.11mmol) was added at room temperature, then the reaction mixture was stirred at reflux temperature for 8 h. After the reaction, the mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> for several times. The organic phase was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and solvent evaporation, the crude product was purified by column chromatography over silica gel with petroleum /  $CH_2Cl_2$  as the eluent to give a yellow solid (1.23 g, 73 %) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.33 (s, 1H), 4.48 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 161.47, 151.07, 145.11, 141.14, 139.03, 130.41, 109.46, 105.55, 100.00, 62.60, 14.27.



### Synthesis of ethyl 4-(4-(diphenylamino)phenyl)thieno[2',3':4,5]benzo[1,2c][1,2,5]thiadiazole-6-carboxylate (BTTTPA)

A mixture of M2 (0.65 g, 1.89 mmol), N, N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.55 g, 4.17 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (78 mg), K<sub>2</sub>CO<sub>3</sub> (3.12 g, 22.57 mmol), THF (40 mL) and deionized water (10 mL) was refluxed at 70 °C for 48 h under Ar<sub>2</sub>. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The CH<sub>2</sub>Cl<sub>2</sub> was removed by vacuum distillation. The crude product was purified by column chromatography over silica gel with petroleum ether / CH<sub>2</sub>Cl<sub>2</sub> as the eluent and then was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> / n-hexane to obtain a red single crystal of BTTTPA. (0.68 g, 71 %).<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 8.41 (s, 1H), 8.18 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 4H), 7.16 (m 8H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 162.20, 153.68, 151.85, 148.51, 147.27, 144.38, 138.91, 136.90, 131.58, 131.00, 130.08, 129.50, 128.64, 125.41, 123.76, 121.88, 112.26, 62.12, 14.34. HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 508.11479, found: 505.11769.





# Synthesis of ethyl 4,8-bis(4-(diphenylamino)phenyl)thieno[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole-6-carboxylate (BTT2TPA)

A mixture of M3 (0.52 g, 1.23 mmol), N, N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.01 g, 2.71 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (65 mg ), K<sub>2</sub>CO<sub>3</sub> (2.05 g, 14.76 mmol ), THF (40 mL) and deionized water (10 mL) was refluxed at 70 °C for 48 h under Ar<sub>2</sub>. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The CH<sub>2</sub>Cl<sub>2</sub> was removed by vacuum distillation. The crude product was purified by column chromatography over silica gel with petroleum ether / CH<sub>2</sub>Cl<sub>2</sub> as the eluent and then was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> / n-hexane to obtain a red single crystal of BTT2TPA (0.60 g, 67%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 8.23 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.28 (m, 24H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 161.95, 151.93, 151.77, 148.74, 147.14, 146.14, 138.60, 136.59, 131.60, 131.01, 130.60, 129.54, 127.92, 125.51, 123.91, 121.68, 103.82, 62.28, 14.33. HRMS (ESI) m/z calcd for C<sub>47</sub>H<sub>35</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>[M+]: 751.21959, found: 751.22106.



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

### 3. Theoretical Calculation



Fig. S1. The optimal geometric construction of BTTTPA and BTT2TPA.

Table S1. Theoretical calculation data of HOMO and LUMO.

Compound	HOMO (eV)	HOMO-1 (eV)	LUMO (eV)	LUMO+1 (eV)
BTTTPA	-5.49	-6.25	-2.81	-1.29
BTT2TPA	-5.25	-5.52	-2.68	-1.21

Excited State	Energy (eV)	Oscillator Strength (a.u.)	Contribution of orbital to Excited States	Weight
S1	2.1237	0.2586	HOMO→LUMO	0.991
S2	2.83	0.0492	HOMO-1→LUMO	0.981
S3	3.5461	0.0827	HOMO→LUMO-1	0.895
			HOMO-4→LUMO-1	0.042
T1	1.359	0.00	HOMO-1→LUMO	0.536
			HOMO→LUMO	0.435
T2	2.2118	0.00	HOMO→LUMO	0.531
			HOMO-1→LUMO	0.399
Т3	2.7584	0.00	HOMO-4→LUMO	0.361
			HOMO-1→LUMO-1	0.29

Table S2. Theoretical calculation data of BTTTPA.

Excited	Energy	Oscillator	Contribution of orbital	Weight
State	(eV)	Strength (a.u.)	to Excited States	
<b>S</b> 1	2.0567	0.398	HOMO→LUMO	0.987
S2	2.3449	0.012	HOMO-1→ LUMO	0.989
S3	2.8193	0.022	HOMO-2→ LUMO	0.987
T1	1.359	0.00	HOMO→LUMO	0.591
			HOMO-2→ LUMO	0.366
T2	2.2118	0.00	$HOMO-1 \rightarrow LUMO$	0.877
			HOMO→LUMO	0.059
Т3	2.7584	0.00	HOMO-4→ LUMO	0.291
			HOMO-1→ LUMO-2	0.213

Table S3. Theoretical calculation data of BTT2TPA.

### 4. Crystal structure Data

 Table S4 Crystal structure data and structure refinement for BTTTPA.

Empirical formula	$C_{29}H_{21}N_3O_2S_2$
Formula weight	507.61
Temperature	108(4) K
Crystal system	triclinic
Space group	P-1
a (Å)	8.8221(2)
b (Å)	9.7361(2)
c (Å)	13.9712(3)
α/°	97.598(2)
β/°	90.425(2)
γ/°	95.061(2)
Volume(Å <sup>3</sup> )	1184.63(4)
Ζ	2
pcalcg/cm <sup>3</sup>	1.423
μ/mm-1	0.259
F(000)	528.0
Crystal size/mm3	0.12×0.11×0.1
$2\Theta$ range for data collection/°	2.942 to 58.906
Index ranges	$-11 \le h \le 11, -13 \le k \le 13, -18 \le l \le 18$
Reflections collected	27101

Data/restraints/parameters	5624/0/326				
Independent reflections	5624 [Rint = 0.0390, Rsigma = 0.0338]				
Goodness-of-fit on F <sup>2</sup>	1.089				
Final R indexes [I>=2σ	$R_1 = 0.0377, wR_2 = 0.0980$				
(I)]					
Final R indexes [all data]	$R_1 = 0.0446, wR_2 = 0.1022$				
Largest diff. peak/hole / e Å <sup>-3</sup>	0.37/-0.31				

Empirical formula	$C_{47}H_{34}N_4O_2S_2$				
Formula weight	750.9				
Temperature	293 K				
Space group	Clcl				
a (Å)	14.9693(6)				
b (Å)	27.0694(10)				
c (Å)	10.1398(5)				
α/°	90				
β/°	99.721(4)				
$\gamma/^{\circ}$	90				
Volume(Å <sup>3</sup> )	4049.8(3)				
Z	4				
μ/mm-1	1.530				
F(000)	1568.0				
Index ranges	$-17 \le h \le 17, -32 \le k \le 32, -12 \le l \le 12$				
Final R indexes [all data]	$R_1 = 0.0899, wR_2 = 0.2688$				

 Table S5 Crystal structure data and structure refinement for BTT2TPA



Fig. S2. The cell stacking of BTTTPA.



Fig. S3. The cell stacking of BTT2TPA.

### 5. Electrochemical Properties



Fig. S4. Cyclic voltammograms (CV) of BTTTPA and BTT2TPA.

### 6. Photophysical Properties



**Fig. S5.** PL spectra of (a) BTTTPA, (b) BTT2TPA and absorption spectra of (c) BTTTPA, (d) BTT2TPA in various solvents (10<sup>-4</sup> M).

Table S6. The photophysical data of BTTTPA and BTT2TPA in different solv	ents.
--	-------

Solvents	З	п	$f(\varepsilon,n)$	BTTTPA			BTT2TPA		
				$\lambda_a$	$\lambda_f$	$v_a$ - $v_f$	$\lambda_a$	$\lambda_f$	$v_a$ - $v_f$
				(nm)	(nm)	(cm <sup>-1</sup> )	(nm)	(nm)	(cm <sup>-1</sup> )
Hexane	1.90	1.375	0.0012	485	581	3407	517	629	3444
<i>p</i> -xylene	2.30	1.496	0.006	492	618	3942	524	640	3459
$CCl_4$	2.24	1.46	0.011	496	604	3605	531	633	3156
Toluene	2.38	1.494	0.014	492	607	3851	527	643	3423
Triethylamine	2.42	1.401	0.048	488	604	3936	521	639	3544
Butyl Ether	3.08	1.399	0.096	488	603	3908	521	642	3617
CB	5.61	1.524	0.143	495	635	4454	530	660	3716
CHCl <sub>3</sub>	4.81	1.443	0.149	495	660	5051	531	667	3840
Ethyl Acetate	6.02	1.372	0.2	482	650	5362	514	659	4281
THF	7.58	1.407	0.21	495	651	4964	519	661	4139
$CH_2Cl_2$	8.93	1.424	0.218	488	666	5476	520	670	4305
DMF	37	1.427	0.276	486	698	6041	516	694	4970
Acetone	20.7	1.359	0.284	480	686	6507	509	679	4918

 $\lambda_a$ = absorption maximum;  $\lambda_f$ = emission maximum;  $v_a$ - $v_f$ = the Stokes shift.

### References

- S. Grimme, S. Ehrlich, L. Goerigk, Effect of the Damping Function in Dispersion Corrected Density Functional Theory, J. Comput. Chem., 2011, 32, 1456-1465.
- X. Gao, S. Bai, D. Fazzi, T. Niehaus, M. Barbatti, W. Thiel, Evaluation of Spin-Orbit Couplings with Linear-Response Time-Dependent Density Functional Methods. J. Chem. Theory Comput., 2017, 13, 515-524.
- 3. T. Lu, F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem., 2012, **33**, 580-592.