Supporting Information

Deep Red/NIR AIEgens based on electron-withdrawing dithiafulvalene-fused benzothiadiazole for solution-processed nondoped OLEDs

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1. General method

1.1 Materials

All reactants and organic solvents are purchased from commercial resources and used without further purification.

1.2 Instruments

NMR spectra were recorded on a Bruker AVANCE NEO 500 NMR spectrometer using CDCl₃ and tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal reference. Highresolution mass spectroscopy (HRMS) was carried out on a GCT premier CAB048 mass spectrophotometer operating in MALDI-TOF mode. UV/vis absorption spectra were recorded on PerkinElmer Lambda 365 UV/vis spectrophotometer. The photoluminescence (PL) spectra were recorded on a Techcomp FL970 spectrofluorometer. The luminescence lifetime was measured on an Edinburgh FLS 980 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900), a microsecond flash-lamp (uF900), and a picosecond pulsed diode laser (EPL-485). Absolute PL quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus QY. Thermogravimetric analysis (TGA) was recorded on a TA TGA55 instrument under a nitrogen atmosphere at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a TA DSC2500 instrument under a nitrogen atmosphere at a heating (cooling) scan rate of 20 °C min⁻¹. Electrochemical measurements were recorded on an Autolab electrochemical workstation in a three-electrode cell using a glassy carbonas the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode as the reference electrode in CH₂Cl₂ with 0.1 M Bu₄N⁺PF₆⁻ at a scan rate of 100 mV s⁻¹ and ferrocene as the internal standard. Scanning electron microscope(SEM) imaging were taken by TESCAN/SOLARIS GMH.

1.3 Synthetic method

Synthesis of intermediates M1, M2, and M3: 4,7-dibromo-5,6difluorobenzo[c][1,2,5]thiadiazole (1 equiv.), (4- (diphenylamino)phenyl)boronic acid (2 equiv.), Pd(PPh₃)₄ (0.1 equiv.), and K₂CO₃ (3 equiv.) were dissolved in dioxane/water (v/v= 5/1). The reaction was heated to reflux for overnight under N₂ atmosphere. The reaction was quenched by adding water. The organic layer was separated, and the solvent was removed by rotary evaporator. The residue was purified by recrystal using dichloromethane/petroleum ether as solvent.

Synthesis of targeting compounds: The product of step 1 (1 equinv.), sodium 2,2dicyanoethene-1,1-bis(thiolate) (10 equiv.), and tetrabutylammonium bromide (32 mg, 2 equiv.) were dissolved in dried dimethylformamide. The reaction was heated at 80 °C for overnight in pressure tube under N_2 atmosphere. The reaction was quenched by adding saturated ammonium chloride solution. The dark red solid was separated by a Buchner funnel. The residue was purified by column chromatography (dichloromethane/petroleum ether) to afford 2TB, 2MTB and 2MOTB.

2. Characterization

2.1 NMR data.



This yellow compound was obtained by step 1 with the yield of 83.54%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.75 (d, *J* = 8.5 Hz,4H), 7.34 (t, *J* = 8.0, 8.0 Hz, 8H), 7.26-7.20 (m, 12H), 7.12 (t, *J* = 7.5 Hz, 4H).



This yellow compound was obtained by step 1 with the yield of 76.85%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.71 (d, *J* = 8.5 Hz, 4H), 7.19-7.11 (m, 20H), 2.37 (s, 12H).



This yellow compound was obtained by step 1 with the yield of 84.72%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.69 (d, *J* = 8.5 Hz, 4H), 7.06 (d, *J* = 8.5 Hz, 8H), 7.19 (d, *J* = 9.0 Hz, 4H), 6.90 (d, *J* = 9.0 Hz, 8H), 3.84 (s, 12H).



This red compound was obtained by step 2 with the yield of 81.48%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.57-7.51 (m, 4H), 7.38 (m, 8H), 7.24-7.19 (m, 4H), 7.30 (m, 4H), 7.28 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 4H) ; ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm):178.25, 153.35, 149.53, 146.79, 145.47, 136.84, 129.91, 129.66, 128.16, 127.11, 125.97, 124.38, 123.48, 120.94, 119.02, 118.88, 112.53.



This red compound was obtained by step 2 with the yield of 52.50%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.49 (m, 4H), 7.23-7.08 (m, 20H), 2.38 (s, 12H) ; ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm): 153.39, 149.86, 144.19, 136.74, 134.20, 130.28, 129.79, 128.17, 126.22, 126.14, 119.74, 112.58, 20.94.



This red compound was obtained by step 2 with the yield of 58.63%.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.47 (d, *J* = 9.0 Hz, 4H), 7.24 (d, *J* = 9.0 Hz, 8H), 7.03 (d, *J* = 9.0 Hz,4H), 6.94 (d, *J* = 9.0 Hz, 8H), 3.85 (s, 12H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm): 156.89, 153.44, 139.57, 136.66, 129.79, 128.18, 127.98, 125.35, 117.99, 115.03, 112.63, 55.52.

2.2 NMR spectra.











Figure S3. ¹H NMR spectrum of M3.



Figure S5. ¹³C NMR spectrum of 2TB.







Figure S7. ¹³C NMR spectrum of 2MTB.





Figure S9. ¹³C NMR spectrum of 2MOTB.

2.3 HRMS

2TB HRMS: m/z calcd for M, 760.1538; found 760.1530.









Figure S11. HRMS spectrum of 2MTB.







3. Supplemental data

3.1 Optical data

Entry	$\lambda_{abs}{}^1$	$2 - \frac{2}{3}/4$ (mm)	$\Phi_{ m F}^{5/6}$ (%)	HOMO ^{7/8}	LUMO ^{7/8}	Lifetime
	(nm)	λ _{em} ⁻¹⁰¹ (ΠΠ)		(eV)	(eV)	(ns)
2TB	480	677/661/691	23.3/33.4	-5.06/-5.10	-2.80/-2.92	6.20
2MTB	500	706/680/702	6.3/11.9	-4.95/-5.16	-2.79/-3.11	2.20
2MOTB	510	N.A./N.A./765	0.2/4.5	-4.82/-5.04	-2.77/-3.06	2.74

Table S1. Summary of the photophysical parameters of the emitters.

N.A = not available.

- 1. The absorption was measured in pure THF.
- 2. The PL data of compounds was measured in pure THF.
- 3. The PL data in aggregate state of compounds was measured in THF/water (1:9) mixture.
- 4. The PL data in solid state was measured in film.
- 5. The quantum yields were measured in THF.
- 6. The quantum yields were measured in film.
- 7. The energy was calculated via theoretic calculation.
- 8. The energy was calculated via CV.

3.2 Solvatochromism



Fig. S13 Solvatochromism of 2TB (a) and 2MTB (b), respectively.

3.3 AIE property



Fig. S14 (a) PL intensity of 2TB in THF/water mixtures. f_w (vol %) is the percentage of volume fraction of water; (b) Plot of I / I_0 of 2TBversus different f_w , wherein, I_0 is the intensity in pure THF.

3.4 Transient decay property



Fig. S15 Time-resolved PL decay spectra of (a) 2TB, (b) 2MTB and 2MOTB (c) at solid state in nanosecond scale at 298 K. 2TB- λ_{ex} = 480 nm, 2MTB- λ_{ex} = 500 nm, and 2MOTB- λ_{ex} = 510 nm, respectively.

3.5 Natural transition orbitals calculation





Fig. S16 Natural transition orbitals (NTO) calculation of 2TB and 2MTB.

3.6 OLED devices data.

Device	Turn-on Voltage ^a (V)	L _{max} ^b (cd m ⁻²)	CE _{max} ^c (cd A ⁻¹)	PE _{max} d (lm W ⁻¹)	EQE _{max} e (%)	λ _{EL} f (nm)
2TB	4.9	419	2.0	1.6	4.9	664
2MTB	4.5	144	0.8	0.6	3.6	690
2MOTB	3.9	8.6	0.006	0.003	0.12	734

Table.S2 Comparison of the EL performance of the devices with 2TB, 2MTB and 2MOTB, respectively.

a. Turn on voltage at a brightness of 1 cd m⁻²; b. Maximum luminance; c. Maximum current efficiency. d. Maximum power efficiency; e. Maximum external quantum efficiency; f. Electroluminescence peak;

3.7 Film morphology.



Fig. S17. SEM pictures of a) 2TB, b) 2MTB and c) 2MOTB films.

3.8 The Crystal data and structure refinement for crystals 2TB and 2MTB.



Fig. S18 Single structure for 2TB



Fig. S19 Single structure for 2MTB

Samples	2TB (CCDC: 2265566)	2MTB (CCDC: 2265565)	
Temperature (K)	293	293	
C-C (Å)	0.0073	0.0164	
Wavelength	0.71073	0.71073	
<i>a</i> (Å)	9.448 (5)	11.897 (5)	
<i>b</i> (Å)	10.025 (5)	13.973 (5)	
<i>c</i> (Å)	22.284 (5)	15.337 (5)	
α (°)	99.685 (5)	103.085 (5)	
β (°)	90.261 (5)	100.283 (5)	
γ (°)	105.301 (5)	97.116 (5)	
Volume	2004.162	2407.316	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C ₄₆ H ₂₈ N ₆ S ₃ , 0.5 (C ₆ H ₁₄)	C ₅₀ H ₃₆ N ₆ S ₃	
Sum formula	C49 H35 N6 S3	C ₅₀ H ₃₆ N ₆ S ₃	
Mr	804.01	817.03	
$Dx (g cm^{-3})$	1.332	1.127	
Z	2	2	
Mu (mm ⁻¹)	0.229	0.192	
F000	838.0	852.0	
F000'	839.00	853.00	
h, k, lmax	13, 14, 31	16, 19, 21	
Nref	12357	14684	
Data completeness	0.616	0.576	
Theta (max)	30.620	30.510	
R (reflections)	0.0808 (5107)	0.3141 (3554)	
wR ₂ (reflections)	0.2698 (7615)	0.6947 (8455)	
S	1.081	2.302	

Table S3. Crystal data and structure refinement for 2TB and 2MTB.

Npar	523	532
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3.9 Literature report.



Fig. S20 The summarized maximum external quantum efficiencies (EQEmax) versus the electroluminescence wavelength in non-doped pure fluorescent OLEDs.