

**Asymmetric Sky-Blue Thermally Activated Delayed
Fluorescence Emitters Bearing Tris(triazolo)triazine Moiety for
Solution Processable Organic Light-Emitting Diodes**

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Experimental part

All synthetic materials are commercial from Energy Chemical Company Ltd. and used in the reaction directly. All reactions were carried out under N₂ atmosphere.

In order to determine the structure of the compound, ¹H NMR and ¹³C NMR spectra were acquired using a Bruker Dex-300/400 NMR instrument using CDCl₃ as a solvent. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of CDCl₃ (δ 7.26 ppm in ¹H NMR, δ 77.0 ppm in ¹³C NMR). Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix.

Thermogravimetric analysis (TGA) was detected with a NETZSCH STA449 from 25°C to 600°C at a 20°C/min heating rate under N₂ atmosphere. To reveal the photophysical properties of emitters, UV-vis absorption spectra were measured by a SHIMADZU UV-1650PC. Steady-state photoluminescence (PL) spectra were obtained with a PTI QuantaMaster 40 steady-state fluorescence spectrofluorometer at room temperature. The luminescence lifetime, low temperature (77 K) fluorescence and phosphorescence spectra of the compounds in solution/film were measured with an Edinburgh FLS1000 transient-fluorescence spectrophotometer. Electrochemical property was evaluated by cyclic voltammetry with three typical electrodes in degassed CH₃CN solution with a rate of 100 mV/s in using a 273A (Princeton Applied Research). The CV system employed Bu₄NPF₆ as electrolyte. Platinum disk was used as the working electrode, platinum wire was regarded as the counter electrode and silver wire was used as the reference electrode. Ferrocenium/ferrocene

(Fc/Fc⁺) was used as the external standard compound. Each oxidation potential was calibrated using ferrocene as a reference.

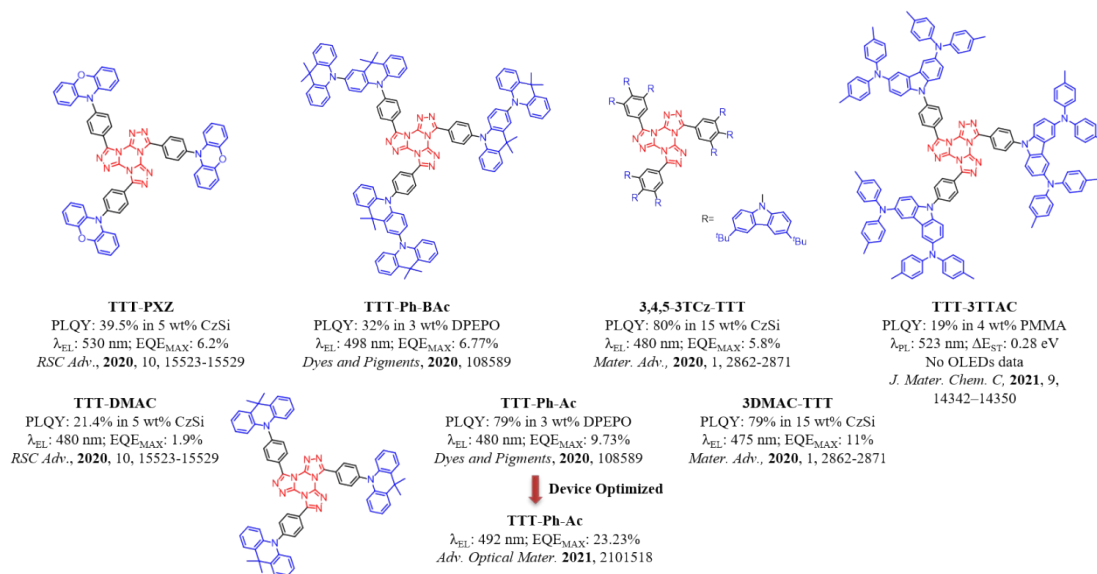


Figure S1. Chemical structures and performances of the reported TTT-based TADF emitters.

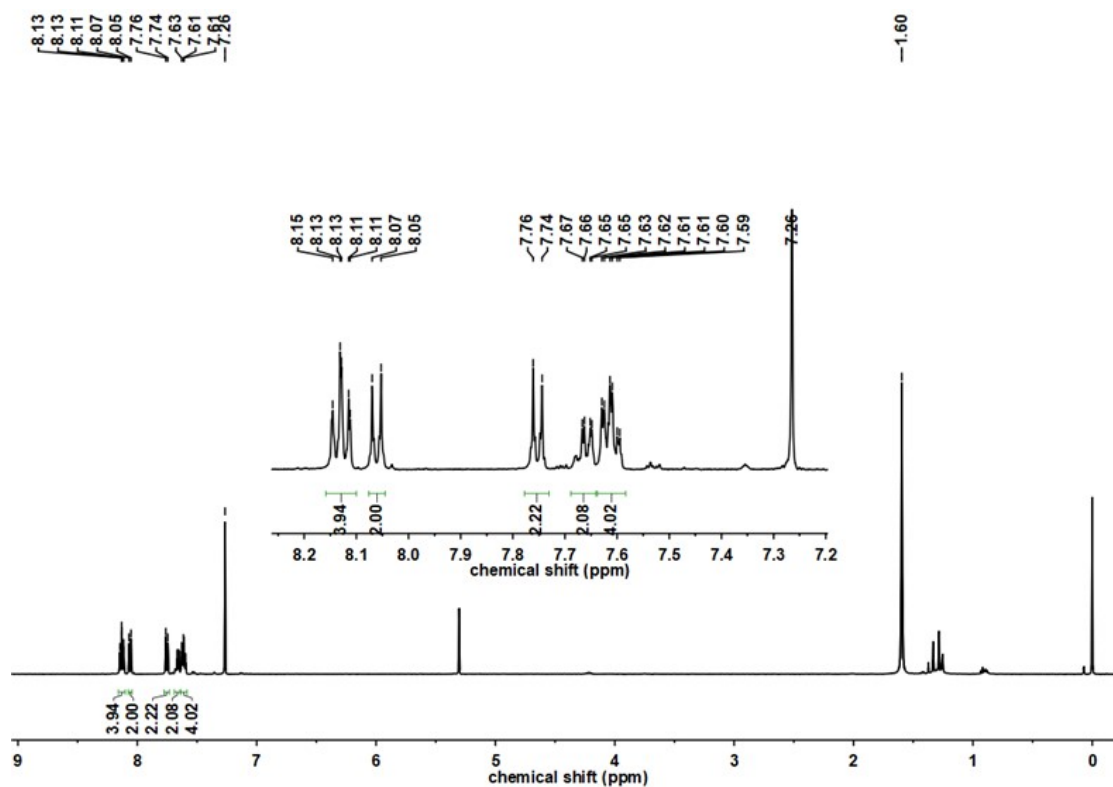


Figure S2. ^1H NMR spectrum of TTT-Br in CDCl_3 .

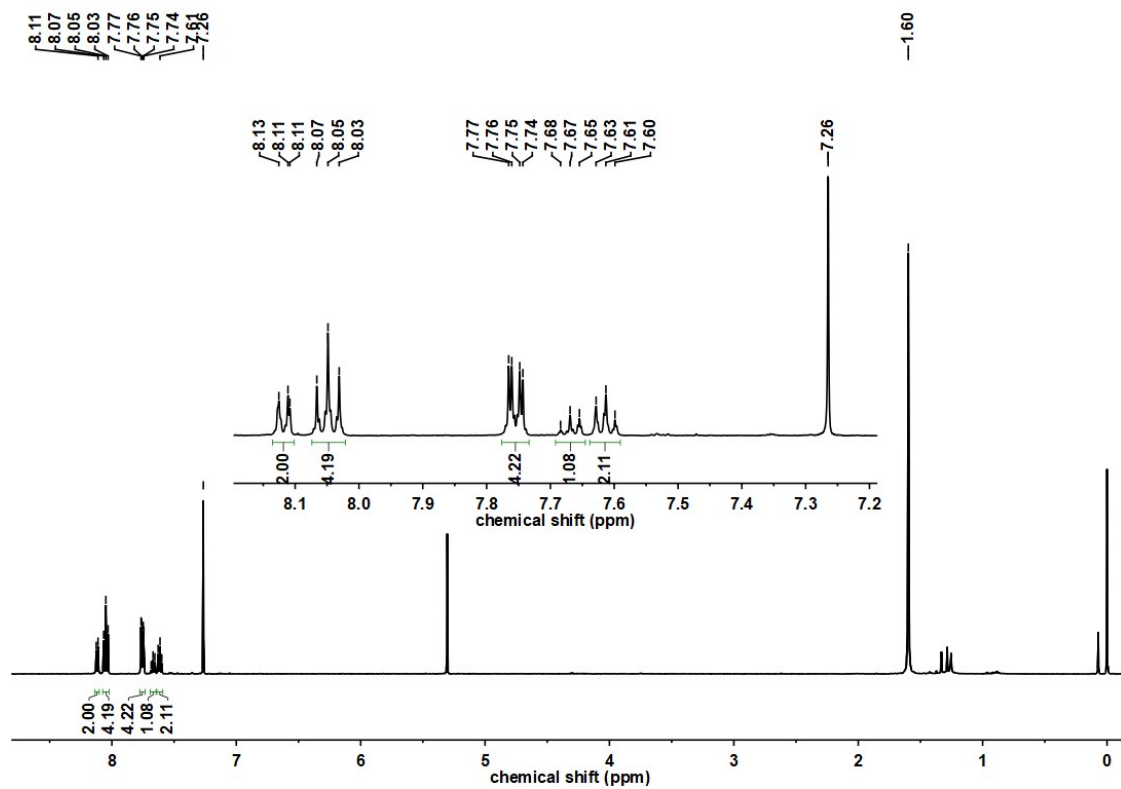


Figure S3. ^1H NMR spectrum of TTT-2Br in CDCl_3 .

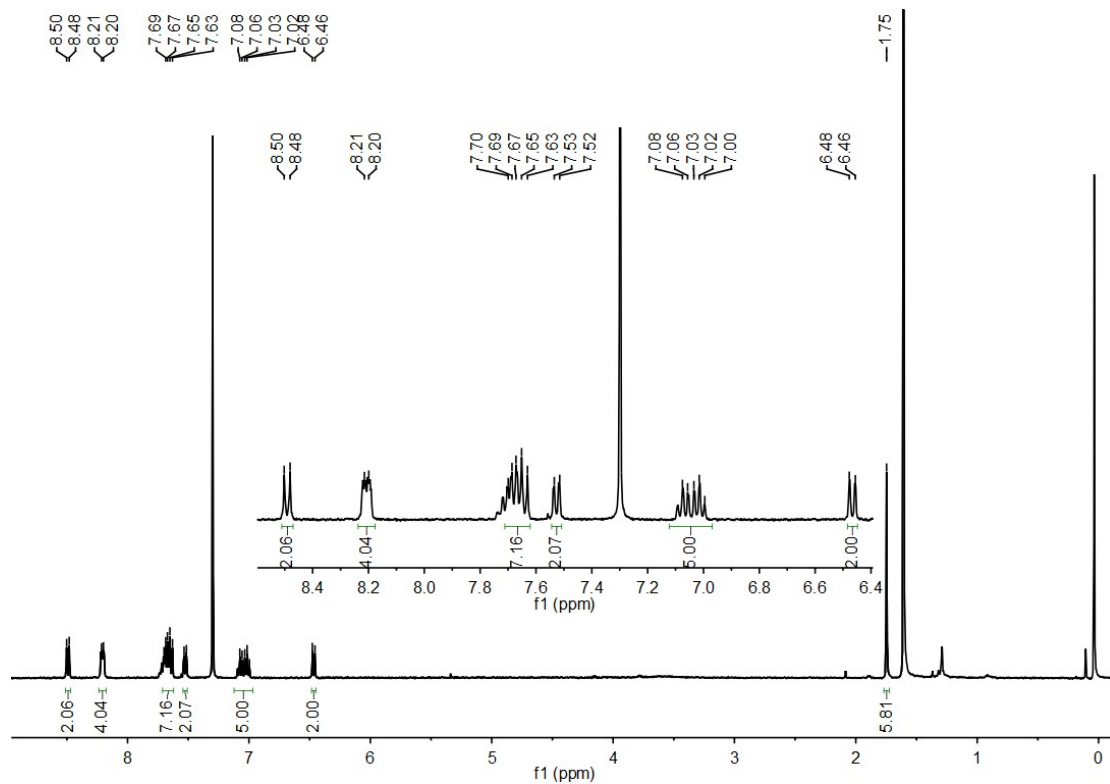


Figure S4. ^1H NMR spectrum of TTT-Ac in CDCl_3 .

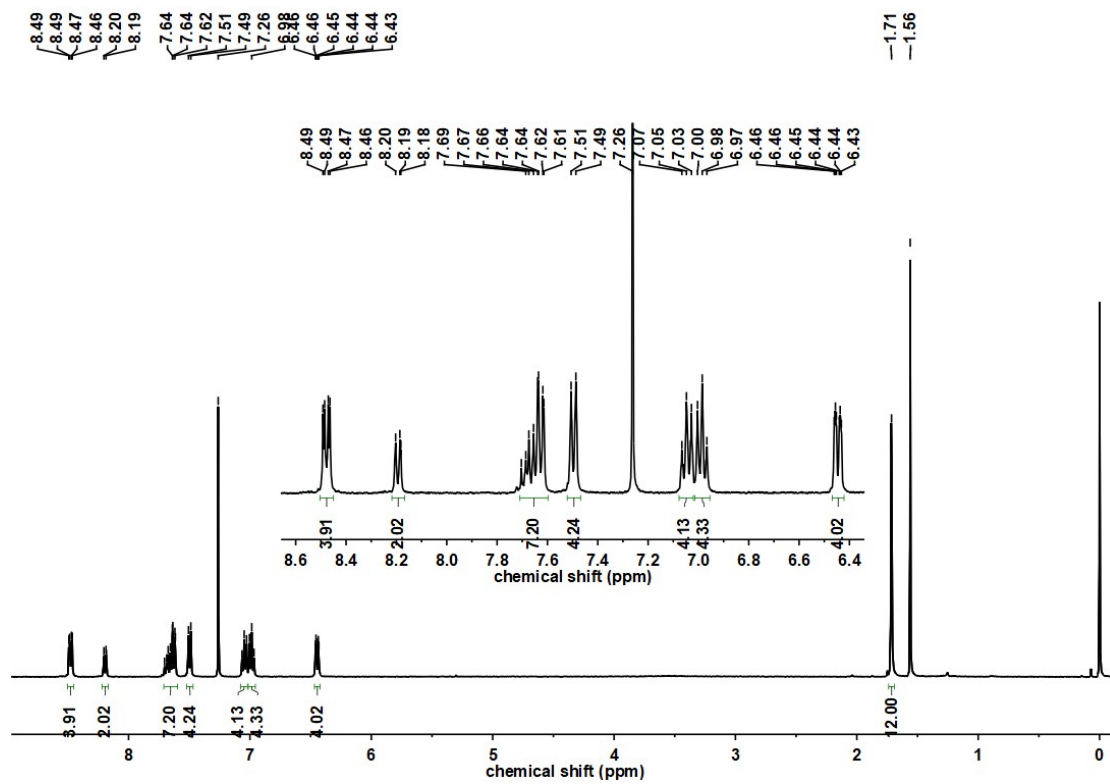


Figure S5. ^1H NMR spectrum of TTT-2Ac in CDCl_3 .

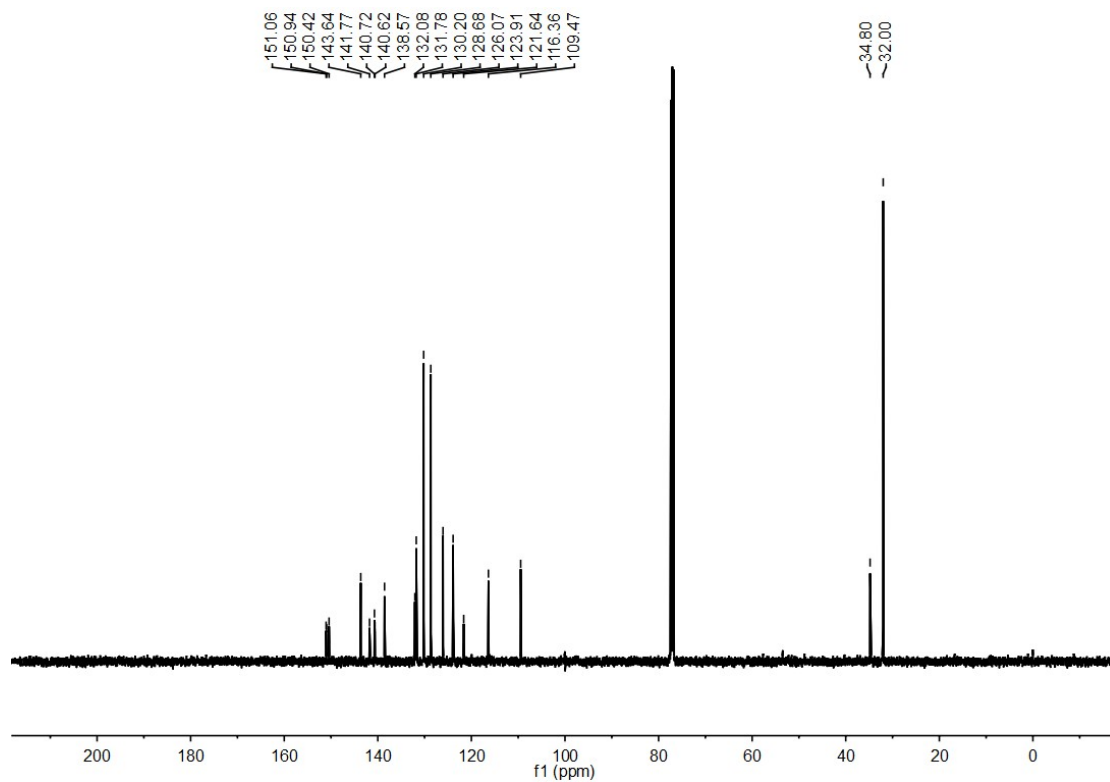


Figure S6. ^{13}C NMR spectrum of TTT-Ac in CDCl_3 .

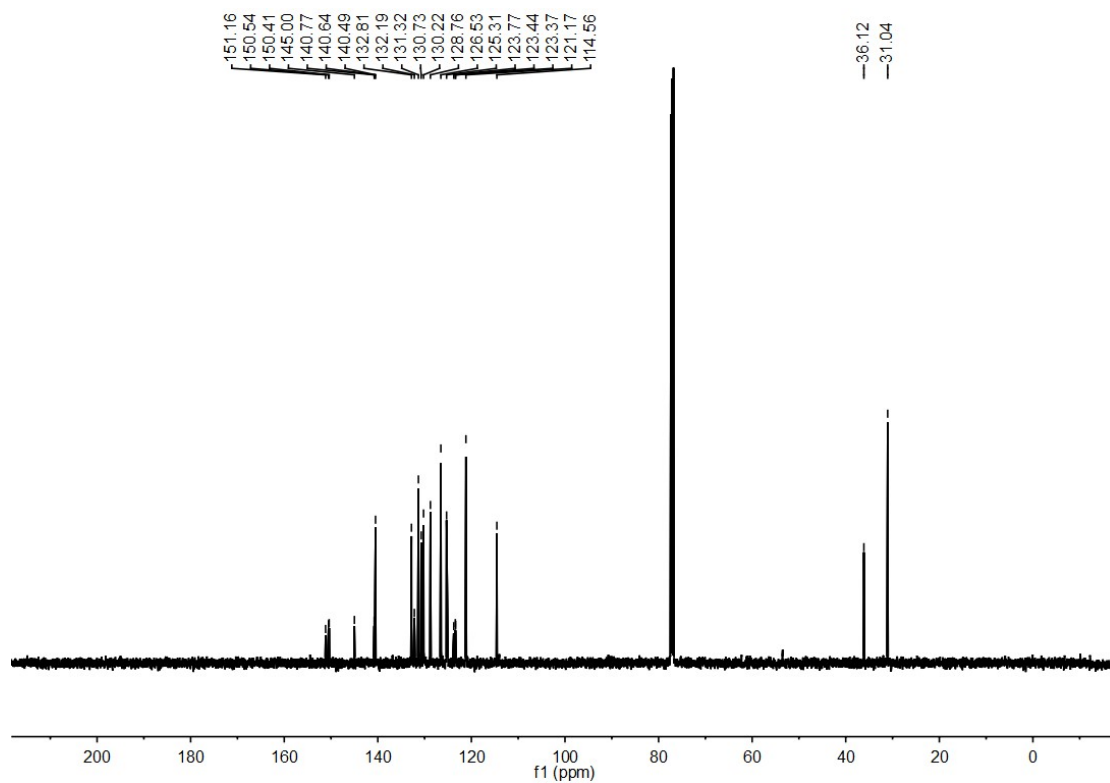


Figure S7. ^{13}C NMR spectrum of TTT-2Ac in CDCl_3 .

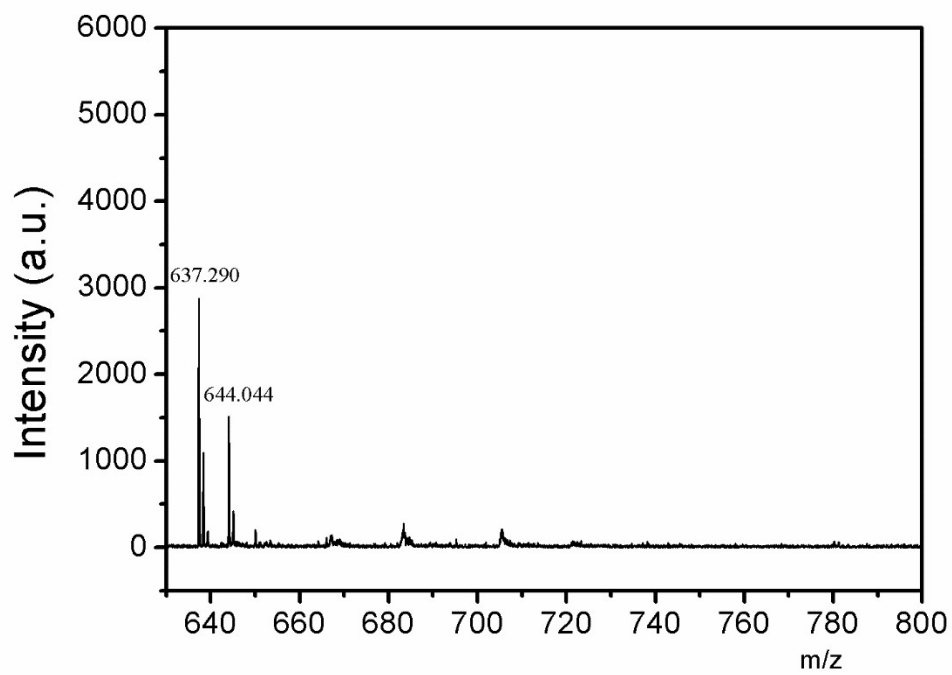


Figure S8. TOF-MS spectrum of TTT-Ac.

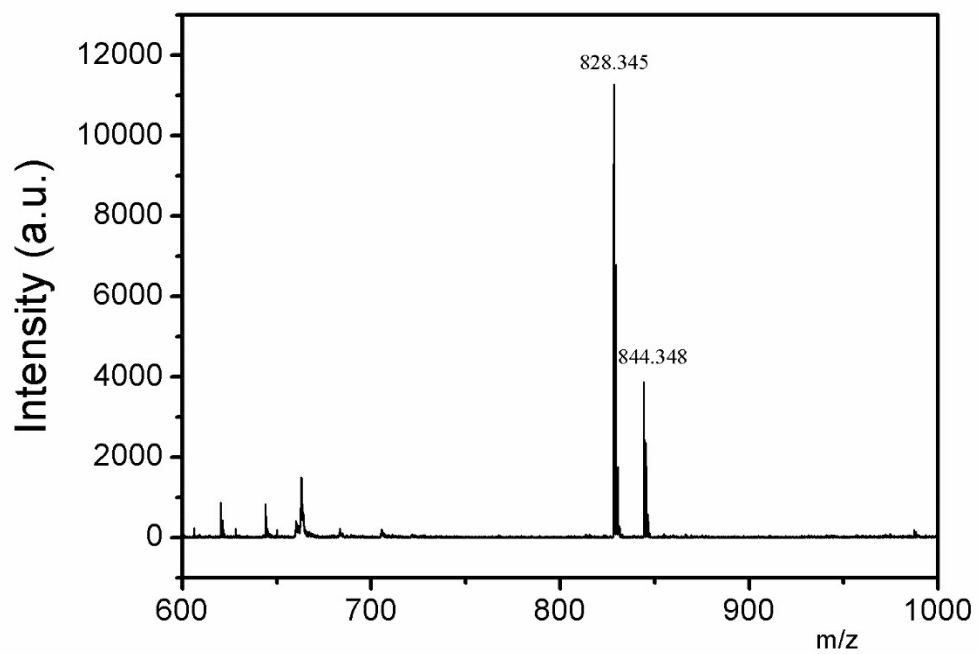


Figure S9. TOF-MS spectrum of TTT-2Ac.

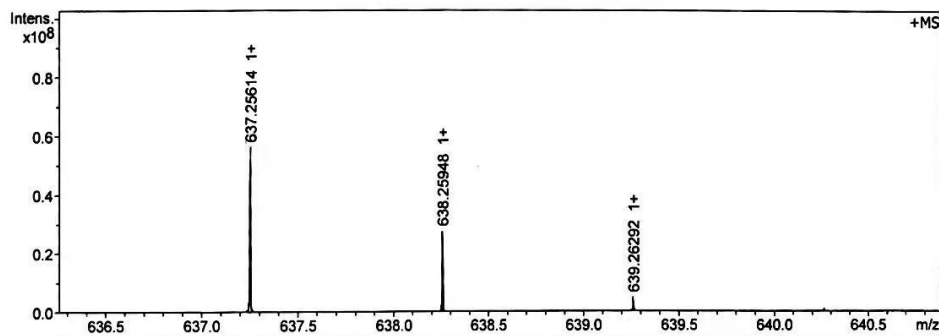
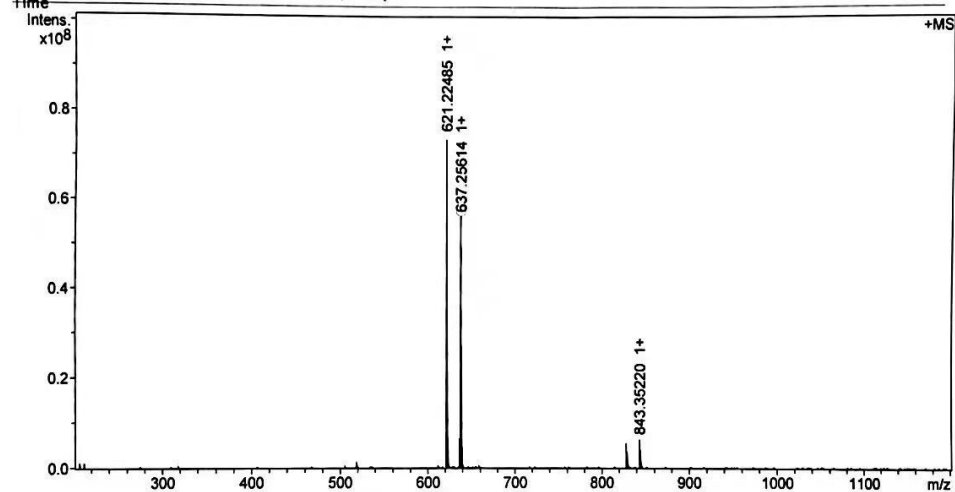
MALDI,TTT-AC,20211213

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 Sample Name MURU-N-ESI Instrument solarix
 Comment

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Accumulation Time	0.100 sec	Frequency			



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Figure S10. HRMS spectrum of TTT-Ac in CH₂Cl₂.

MALDI, TTT-ZAC, 20211213

Analysis Info

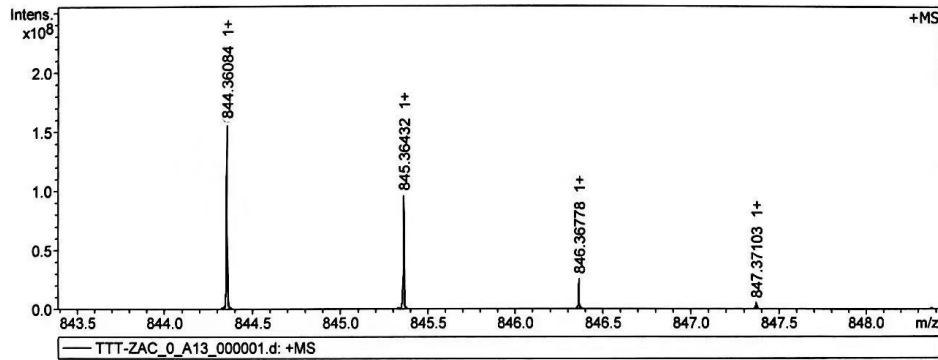
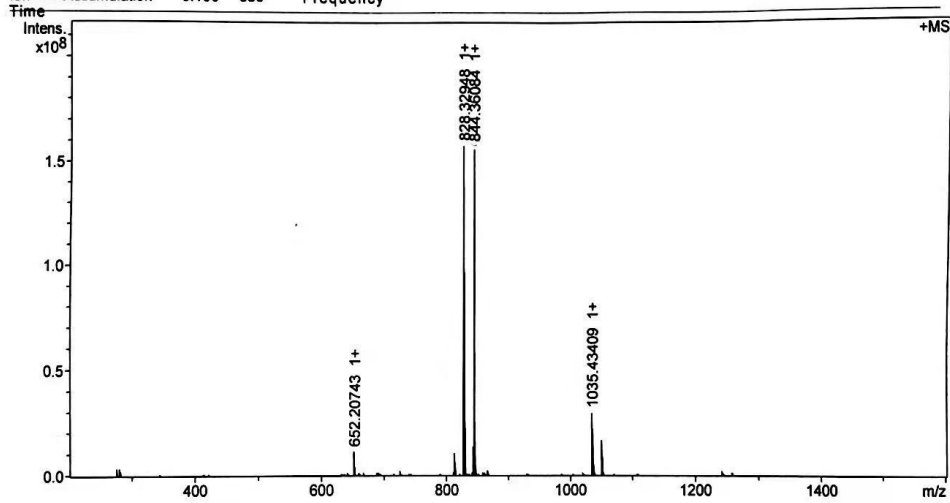
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Operator
Instrument solarix

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Broadband High	1600.0 m/z	Laser Power	18.8 lp	Ionization	Sine-Bell Multiplication
Source	0.001 sec	Laser Shot	0.020 sec		
Accumulation	0.100 sec	Frequency			



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Figure S11. HRMS spectrum of TTT-2Ac in CH₂Cl₂.

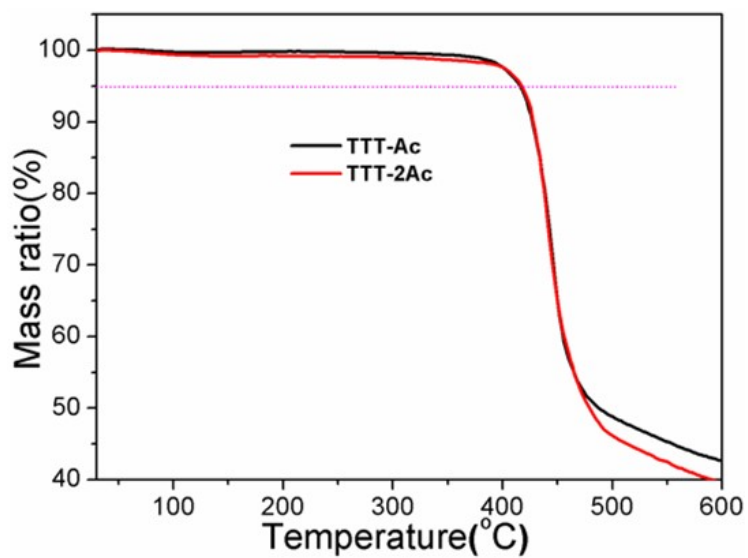


Figure S12. TGA curves of the compounds at N_2 atmosphere with a heating rate of $20^\circ C \text{ min}^{-1}$.

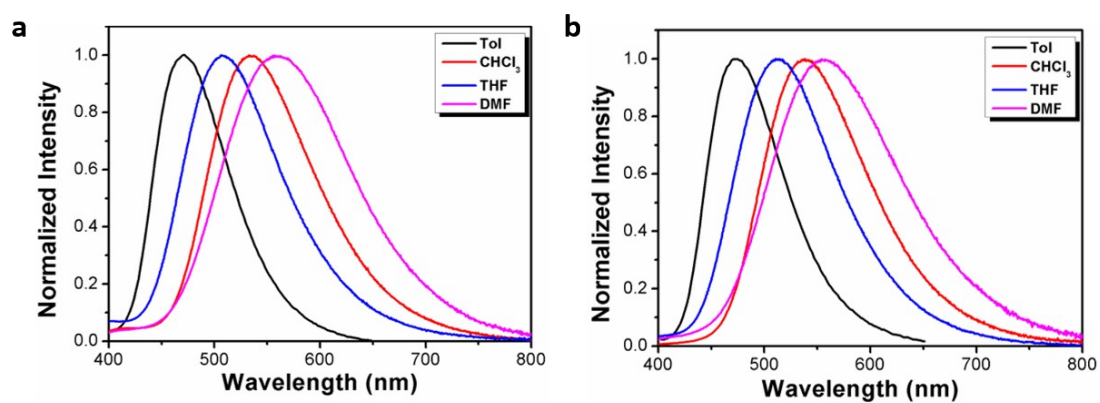


Figure S13. PL spectra of TTT-Ac (a) and TTT-2Ac (b) in different solvents at room temperature.

Table S1. Calculated Photophysical data of the TADF emitters.

Compound	τ_p/Φ_p (ns/%)	τ_d/Φ_d (μ s/%)	k_p (10^7 s ⁻¹)	k_d (10^4 s ⁻¹)	k_{ISC} (10^7 s ⁻¹)	k_{rISC} (10^4 s ⁻¹)	k_r (10^7 s ⁻¹)	k_{nr} (10^4 s ⁻¹)
TTT-Ac	10.9/21	27.2/42	9.17	3.68	7.24	9.32	1.93	1.72
TTT-2Ac	11.9/10	20/37	8.4	5	7.56	20.55	0.84	2.95

$$k_p = 1/\tau_p \quad (1)$$

$$k_d = 1/\tau_d \quad (2)$$

$$k_{ISC} = (1-\Phi_p)k_p \quad (3)$$

$$k_{rISC} = k_p k_d \Phi_d / k_{ISC} \Phi_p \quad (4)$$

$$k_r = \Phi_p / \tau_p \quad (5)$$

$$k_{nr} = k_d - \Phi_p k_{rISC} \quad (6)$$

Herein, τ_p and τ_d are the lifetime of prompt and delayed components. Φ_p and Φ_d are the prompt and delayed luminescence quantum efficiency, respectively. The k_p and k_d are the rate constant of prompt and delayed fluorescence. k_{ISC} is the rate constant of intersystem crossing, while k_{rISC} is the rate constant of reverse intersystem crossing between the S_1 and T_1 . k_r and k_{nr} are the radiative and nonradiative decay rate constant from S_1 to S_0 , respectively.

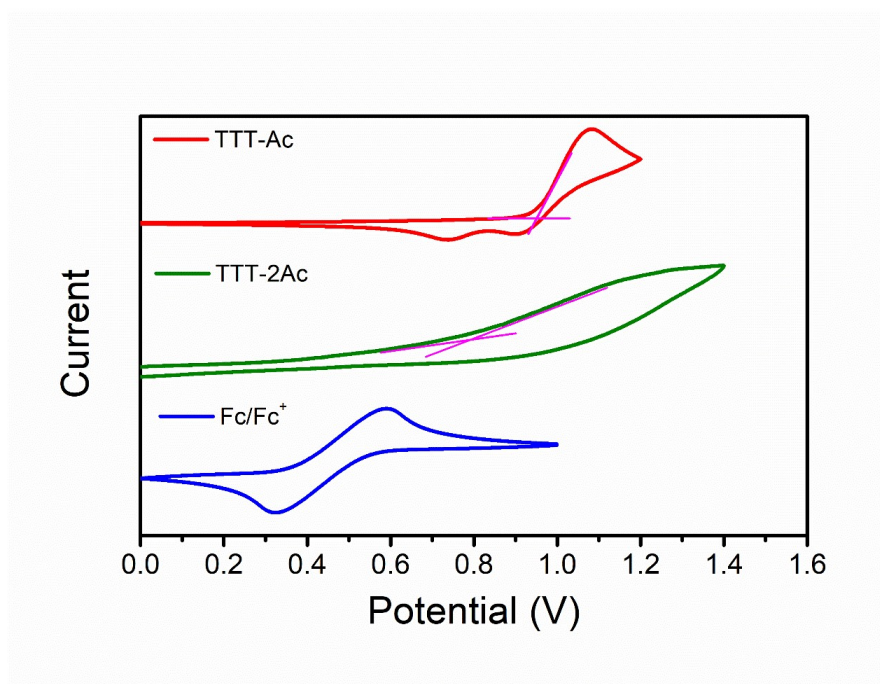


Figure S14. CV curves of compounds in CH₃CN solution.

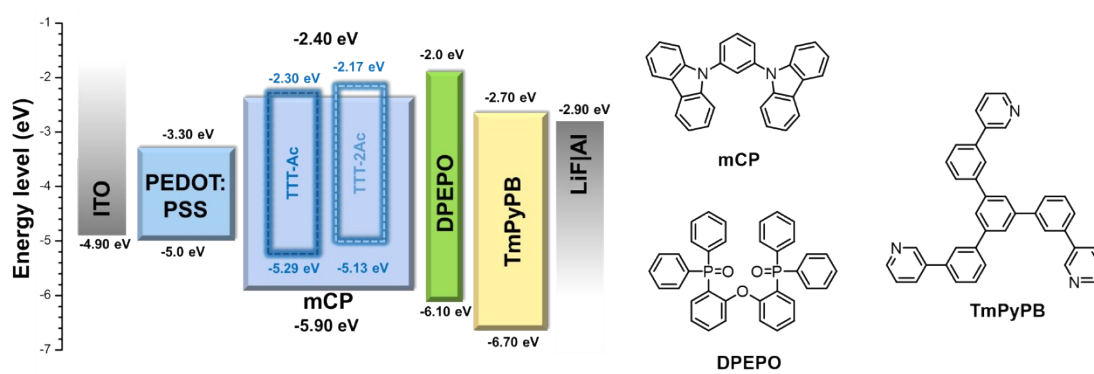


Figure S15. The energy level diagrams and chemical structures of the materials in the devices.

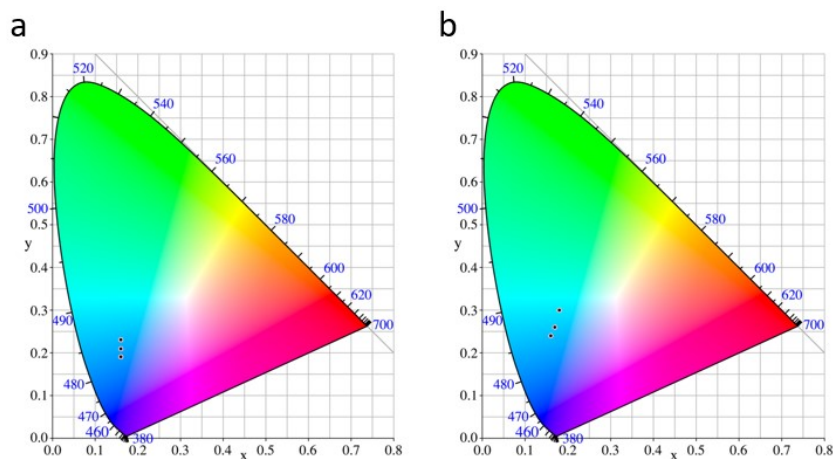


Figure S16. CIE coordinates of the devices: (a): TTT-Ac; (b) TTT-2Ac.

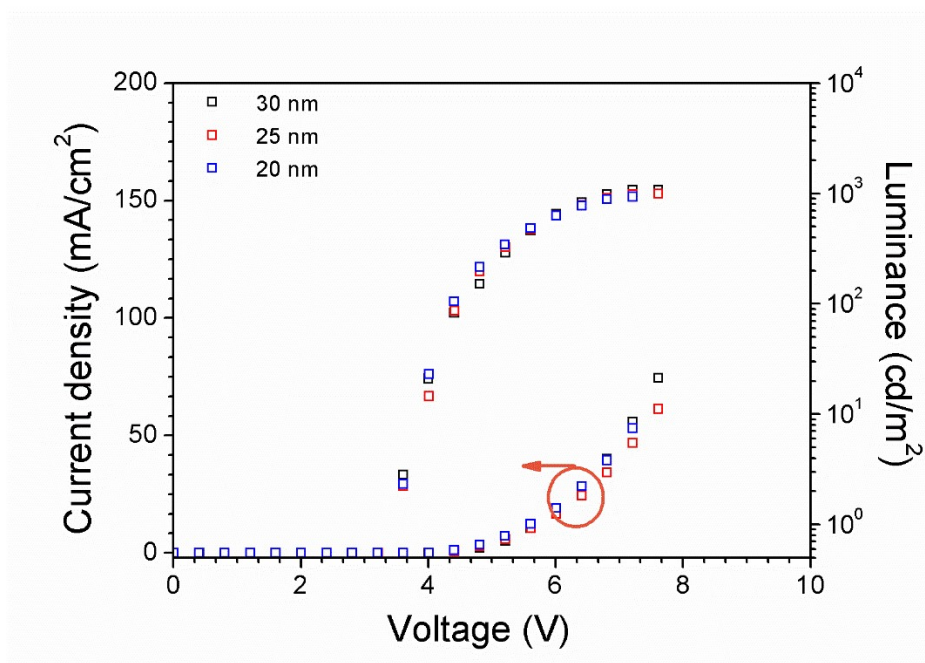


Figure S17. Current density-voltage-luminance (J-V-L) curves (c) of TTT-Ac with different EML thickness of 20 wt% dopants.

Table S2. EL data for the devices with different EML thickness.

Material	EML Thickness (nm)	Dopant wt%	V_{ON} V	L_{max} cd m ⁻²	CE_{max} cd A ⁻¹	EQE_{max} %	CIE (x, y)	Peak nm
TTT-Ac	30	20%	3.6	1078	16.21	9.26	(0.16 , 0.21)	470
	25	20%	3.6	996.4	17.37	10.01	(0.16 , 0.22)	474
	20	20%	3.6	935.3	14.52	8.48	(0.16 , 0.23)	470

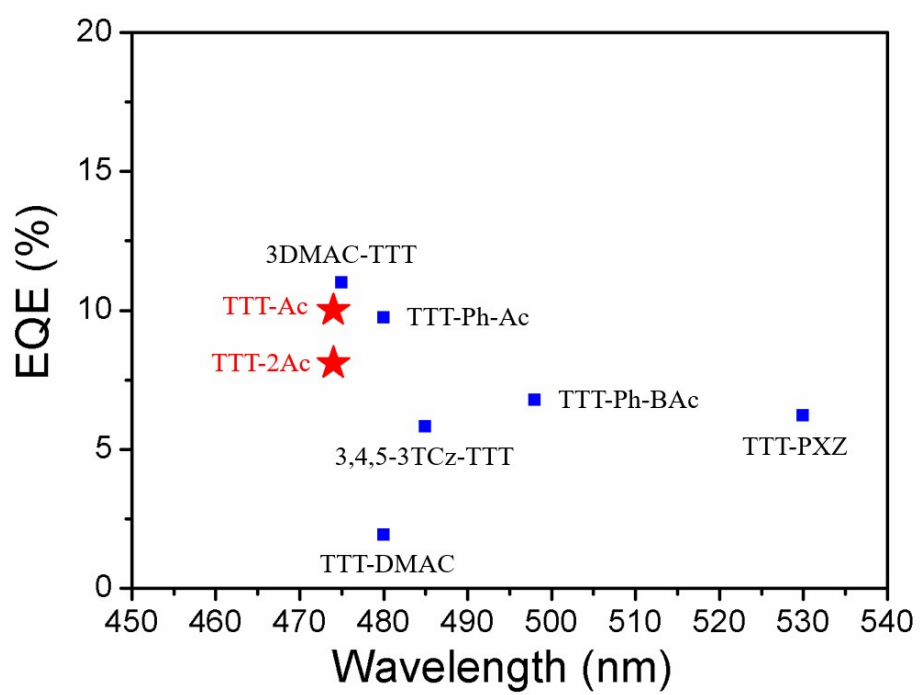


Figure S18. EQE-wavelength curves of the TTT-based TADF emitter.