Electronic Supplementary Information (ESI)

Fused Twin-Acridine Scaffold as Electron Donor for Thermally Activated Delayed Fluorescence Emitters: Controllable TADF Behavior by Methyl Substitution

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Experimental

S1. General information

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Dimethyl 4,6-dibromoisophthalate (compound 1) and 6,12,12,14,14-pentamethyl-5,7,12,14-tetrahydroquinolino[3,2-b]acridine (MeTMQAC) were synthesized according to the literature^{1,2}. All the reaction solvents were purified by solvent purification system prior to use.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded in deuterated dimethylsulfoxide (DMSO- d_6) and chloroform (CDCl₃) solution on Bruker NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CDCl₃: δ 7.26, DMSO- d_6 : δ 2.50 for ¹H, and 77.16 for ¹³C at room temperature). High-resolution electrospray (ESI) mass spectra were performed on SCIEX TripleTOF6600 nanoLCMS. Thermal gravity analysis (TGA) was performed on a TA TGA 55 instrument. Differential scanning calorimetry (DSC) was performed on a TA DSC 25 from 40 to 300 °C under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of 10 °C min⁻¹. UV-vis absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The transient photoluminescence decay curves were measured by a single photo counting spectrometer from Edinburgh Instruments (FLS920).

Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics). Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (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 pseudoreference electrode with ferroceniumferrocene (Fc⁺/Fc) as the internal standard.

Device Fabrication:

Indium tin oxide (ITO) with a sheet resistance of 15 Ω square⁻¹ was used as the substrate. Prior to use, the ITO glass substrates were pre-cleaned carefully and treated by oxygen plasma for 5 min before device fabrication. Then the sample was transferred to the deposition system. All organic layers were deposited at a rate of 1 Å s⁻¹, and subsequently Liq was deposited at 0.2 Å s⁻¹ and then capped with Al (*ca.* 4 Å

s⁻¹) through a shadow mask in a vacuum of 2×10^6 Torr. For all the OLEDs, the emitting areas were determined by the overlap of two electrodes as 0.09 cm². The EL spectra, CIE coordinates and *J*–*V*–*L* curves of the devices were measured with a PHOTO RESEARCH SpectraScan PR 655 photometer and a KEITHLEY 2400 SourceMeter constant current source. The EQE values were calculated according to previously reported methods. All measurements were carried out at room temperature under ambient conditions.

S2. Synthesis of materials



Dimethyl 4,6-bis(phenylamino)isophthalate (2): A mixture of aniline (1.12 g, 12 mmol), dimethyl 4,6-dibromoisophthalate (1) (3.52 g, 10 mmol), Pd(OAc)₂ (0.22 g, 1 mmol), Cs₂CO₃ (13.00 g, 40 mmol), (t-Bu)₃PHBF₄ (0.75 g, 2.6 mmol) and 20 mL toluene were stirred and refluxed for 24 h under argon. After cooling to room temperature, the reaction mixture was filtered through celite pad and washed with DCM. The combined organic phase was dried over with anhydrous Na₂SO₄, followed by concentrating under reduced pressure. The residue was purified by column chromatography on silica gel using DCM/petroleum ether (v/v = 1/1) as the eluent to obtain the product as a white powder. Yield: 78%. ¹H NMR (500 MHz, DMSO-*d*₆) δ [ppm]: 9.70 (s, 1H), 8.58 (s, 1H), 7.35 (t, J = 7.8 Hz, 4H), 7.25 (d, J = 7.6 Hz, 4H), 7.10 (t, J = 7.3 Hz, 2H), 6.66 (s, 1H), 3.84 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ [ppm]: 168.38, 151.89, 139.67, 138.09, 129.34, 124.46, 123.30, 102.74, 94.17, 51.69. HRMS (ESI): m/z [M+H]⁺, calculated for C₂₂H₂₀N₂O₄: 377.1496; found: 377.1509.



12,12,14,14-tetramethyl-5,7,12,14-tetrahydroquinolino[3,2-b]acridine

(TMQAC): Compound 2 (2.26 g, 6.00 mmol) was dissolved in 40 mL dry THF, then cooled and stirred at -78 °C for 20 min under argon. Then methyllithium (36 mL, 36 mmol) was added dropwise to the mixture and kept -78 °C for another 2 hours. The reaction mixture was gradually warmed to room temperature and quenched with saturated ammonium chloride (2M) and extracted with DCM. The organic phase was dried with anhydrous Na₂SO₄. After filtering and concentrating under reduced pressure, the crude diol intermediate was dissolved in 10 mL dry DCM under argon atmosphere. 10 mL of boron trifluoride ethyl ether were added dropwise, and the mixture was then neutralized with NaOH (2M) and extracted with DCM three times. The combined organic phase was dried with anhydrous Na₂SO₄ and concentrating under reduced pressure. The crude product was purified by column chromatography on silica gel using DCM/petroleum ether ($\nu/\nu = 1/3$) as the eluent to obtain the product as a white powder (1.24 g, yield: 72%). ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm]: 8.69



(s, 2H), 7.31 (dd, J = 8.1, 1.5 Hz, 1H), 7.26 (s, 1H), 7.07 – 6.92 (m, 2H), 6.81 – 6.65 (m, 4H), 6.19 (s, 1H), 1.48 (s, 12H). ¹³C NMR (125 MHz, DMSO- d_6) δ [ppm]: 138.95, 137.18, 128.45, 126.31, 125.43, 122.38, 120.18, 119.01, 113.13, 97.13, 35.28, 31.66. HRMS (ESI): m/z [M+H]⁺, calculated for C₂₄H₂₄N₂: 341.2012; found: 341.2016. **General synthesis of Emitters:** A mixture of the donor (1 mmol), aryl bromide (2.4)

mmol), $Pd(OAc)_2$ (22.50 mg, 0.1 mmol), *t*-BuONa (0.38 g, 4 mmol), (*t*-Bu)₃PHBF₄

(75.40 mg, 0.26 mmol) and 20 mL toluene were stirred and refluxed for 24 h under argon. After cooling to room temperature, the reaction mixture was filtered through celite pad and washed with DCM. The organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using DCM/petroleum ether (v/v = 1/1) as the eluent to obtain the product.

TRZ-TMQAC: Using TMQAC and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine as the coupling partner. The product is obtained as a green powder. Yield: 72%. ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.69 (d, *J* = 8.4 Hz, 4H), 8.35 (dd, *J* = 8.2, 1.4 Hz, 8H), 7.54 (s, 1H), 7.50-7.43 (m, 2H), 7.37 (t, *J* = 7.3 Hz, 4H), 7.26 (q, *J* = 7.2, 6.7 Hz, 12H), 6.91-6.87 (m, 4H), 6.28– 6.24 (m, 2H), 5.08 (s, 1H), 1.77 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ [ppm]: 171.09, 170.41, 145.12, 140.26, 130.31, 135.97, 135.65, 132.29, 131.25, 131.10, 128.81, 128.28, 126.45, 122.89, 122.56, 120.49, 113.89, 101.046, 35.79, 32.63. HRMS (ESI): *m*/*z* [M + H]⁺ calculated for C₆₆H₅₀N₈: 955.4231; found: 955.4204.

DPS-TMQAC: It was prepared by the same procedure with **TRZ-TMQAC** except using 1-bromo-4-(phenylsulfonyl)benzene as the coupling partner. Product is obtained as a white powder. Yield: 73%. ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.07-8.09 (m, 4H), 7.91 (d, J = 8.5 Hz, 4H), 7.60-7.66 (m, 6H), 7.49 (s, 1H), 7.42-7.44 (m, 2H), 7.25 (d, J = 8.5 Hz, 4H), 6.96-7.0 (m, 4H), 6.34-6.36 (m, 2H), 5.78 (s, 1H), 1.62 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ [ppm]: 147.126, 141.427, 140.502, 139.275, 138.574, 133.931, 133.572, 129.886, 129.654, 128.063, 127.916, 126.460, 125.335, 122.423, 122.187, 117.206, 105.349, 36.349, 30.803. HRMS (ESI): m/z [M + H]⁺ calculated for C₄₈H₄₀N₂O₄S₂: 773.2502; found: 773.2488.

TRZ-MeTMQAC: By using MeTMQAC and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5triazine as the coupling partner, the product was obtained as yellow solid. Yield: 78%. ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.715-8.753 (m, 12H), 7.668 (d, J = 7.5 Hz, 2H), 7.455-7.545 (m, 15H), 7.353 (t, J = 7.5 Hz 1H), 7.238-7.276 (m, 7H), 2.372 (s, 3H), 1.581 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ [ppm]: 171.409, 149.468, 145.320, 142.771, 142.459, 139.690, 136.692, 132.309, 131.662, 130.858, 128.956, 128.712, 127.507, 127.261, 126.084, 125.921, 124.533, 117.892, 113.322, 39.067, 27.545, 14.831. HRMS (ESI): m/z [M + H]⁺ calculated for C₆₇H₅₂N₈: 969.4388; found: 969.4369.

DPS-MeTMQAC: By using MeTMQAC and 1-bromo-4-(phenylsulfonyl)benzene as the coupling partner, the product is obtained as a white powder. Yield: 78%. ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 7.96 (d, J = 6.9 Hz, 4H), 7.778 (d, J = 9.0 Hz, 4H), 7.445-7.560 (m, 12H), 7.207-7.305 (m, 4H), 7.03 (d, J = 8.8 Hz, 4H), 1.473 (s, 3H), 2.140 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ [ppm]: 149.388, 145.128, 143.171, 142.663, 141.631, 139.150, 132.847, 129.690, 129.333, 127.511, 126.277, 124.755, 118.278, 113.042, 39.056, 14.682. HRMS (ESI): m/z [M + H]⁺ calculated for C₄₉H₄₂N₂O₄S₂: 787.2659; found: 787.2634.



Fig. S1 ¹H NMR spectrum of compound 2.



Fig. S2 ¹³C NMR spectrum of compound 2.





145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0



















Fig. S13 TGA thermograms of emitters recorded at a heating rate of 10°C/min.



Fig. S14 The optimal geometric construction, molecular frontier orbital distributions of DPS-TMQAC and DPS-MeTMQAC obtained by theoretical calculations.

Compounds	HOMO [eV] ^c	LUMO [eV]	S ₁ [eV]	T ₁ [eV]	$\Delta E_{\rm ST}$ [eV]	f
TRZ-TMQAC	-4.86	-2.19	2.41	2.40	0.01	0.0037
TRZ-MeTMQAC	-5.21	-2.02	2.60	2.93	0.33	0.0088
DPS-TMQAC	-5.02	-1.53	3.11	2.93	0.18	0.0004
DPS-MeTMQAC	-5.28	-1.59	2.84	3.31	0.47	0.0369



Fig. S15 Cyclic voltammograms of emitters in dichloromethane for oxidation.



Fig. S16 Fluorescence spectra of TMQAC-based emitters in different solvent.



Fig. S17 UV-vis and fluorescence spectra of DPS-TMQAC and DPS-MeTMQAC in toluene solution.



Fig. S18 Optical properties of DPS-TMQAC and DPS-MeTMQAC, **a**) fluorescence at 300 K and phosphorescence at 77K of 10 wt.% emitters doped into the DPEPO host, **b**) and **c**) The transient photoluminescence decay curves of emitters in toluene (10⁻⁵ M) under degassed and aerated condition.



Fig. S19 The transient photoluminescence decay curves of emitters in doped film under degassed and aerated condition.



Fig. 20 OLEDs characteristics of MeTMQAC-based devices, (a) EQE, CE, PEcurrent density curves. (b) Luminescence and (d) current density versus voltage characteristics.

Emitters	V _{on} [V] ^a	λ _{em} [nm]	PE ^b [lm/W]	CE ^b [cd/A]	EQE ^b [%]	L _{max} [cd/m ²]	CIE ^c (x,y)
TRZ-TMQAC	3.0	522	51.9/44.7/26. 6	66.1/64.1/50.1	20.7/20.1/16.0	18400	0.30, 0.56
TRZ- MeTMQAC	3.0	480	6.5/4.2/1.4	8.3/6.6/3.8	5.5/4.4/2.5	3100	0.18, 0.26
DPS-TMQAC	3.0	486	21.3/21.3/8.9	30.5/30.5/18.5	14.3/14.3/8.4	4300	0.19, 0.33
DPS-MeTMQAC	3.0	450	2.0/0.1/-	1.9/0.2/-	1.2/0.1/-	200	0.21, 0.18

Table S2. Summary of the OLED device data.

^{*a*} Turn-on voltage (at a brightness of 1 cd/m²). ^{*b*} The order of measured value: maximum, then values at the brightness of 100 and 1000 cd/m². ^{*c*} Commission International de l'Eclairage coordinates

References

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