**Electronic Supplementary Information (ESI)** 

## A Simple and Effective Strategy to Lock the Quasi-Equatorial Conformation of

# Acridine by H-H Repulsion for Highly Efficient Thermally Activated Delayed

### **Fluorescence Emitters**

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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. All the reaction solvents were purified by solvent purification system prior to use.

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded in deuterated dimethylsulfoxide (DMSO- $d_6$ ) and chloroform (CDCl<sub>3</sub>) 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 (CDCl<sub>3</sub>:  $\delta$  7.26, DMSO- $d_6$ :  $\delta$  2.50 for <sup>1</sup>H, and 77.16 for <sup>13</sup>C 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<sup>-1</sup>. UVvis 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 PicoQuant (FluoTime 300).

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 (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<sup>+</sup>/Fc) as the internal standard.

#### **Device Fabrication:**

Indium tin oxide (ITO) with a sheet resistance of 15  $\Omega$  square<sup>-1</sup> 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<sup>-1</sup>, and subsequently Liq was deposited at 0.2 Å s<sup>-1</sup> and then capped with Al (*ca.* 4 Å s<sup>-1</sup>) through a shadow mask in a vacuum of 2×10<sup>6</sup> Torr. For all the OLEDs, the emitting areas were determined by the overlap of two electrodes as 0.09 cm<sup>2</sup>. 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 2,2'-(1,3-phenylenebis(azanediyl))dibenzoate (1)**: A mixture of 1,3dibromobenzene (2.36 g, 10 mmol), methyl 2-aminobenzoate (3.62 g, 24 mmol), Pd(OAc)<sub>2</sub> (0.22 g, 1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (13.00 g, 40 mmol), (t-Bu)<sub>3</sub>PHBF<sub>4</sub> (0.75 g, 2.6 mmol) and 30 mL dry 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 Na<sub>2</sub>SO<sub>4</sub> and 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 as a white powder. Yield: 76%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]:  $\delta$  9.46 (s, 2H), 7.96 (dd, J = 8.1, 1.4 Hz, 2H), 7.37 – 7.21 (m, 6H), 6.96 (dd, J = 8.0, 2.0 Hz, 2H), 6.74 (dd, J = 8.2, 6.3, 1.8 Hz, 2H), 3.90 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 169.27, 147.97, 142.36, 134.51, 132.01, 130.53, 117.73, 117.60, 115.92, 114.83, 112.57, 52.20. HRMS (ESI): m/z [M+H]<sup>+</sup>, calculated for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: 377.1496; found: 377.1494.



#### 8,8,14,14-tetramethyl-5,8,13,14-tetrahydrodibenzo[b,j][1,7]phenanthroline

(TMDBP): Compound 1 (1.88 g, 5.00 mmol) was dissolved in 20 mL dry THF and cooled to -78 °C for 20 min under argon. Then methyllithium (36 mL, 1M, 36 mmol) was added dropwise to the mixture and stirred at -78 °C for another 2 hours. The reaction mixture was gradually warmed to room temperature and quenched with ammonium chloride solution (2M) and extracted with DCM three times. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtering and concentrating under reduced pressure, the crude diol intermediate was dissolved in 10 mL dry DCM under argon atmosphere, and 10 mL of boron trifluoride ethyl ether were added dropwise. The mixture was further stirred at room temperature for 12 hours under argon. The reaction mixture was then neutralized with NaOH (2M) and extracted with DCM three times. The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using DCM/petroleum ether (v/v = 1/3) as the eluent to obtain the product as a white powder. Yield: 50%. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  [ppm]: 8.60 (s, 1H), 7.34 (ddd, J = 13.2, 7.9, 1.4 Hz, 2H), 7.26 (dd, J = 8.0, 1.2 Hz, 1H), 7.16 – 7.04 (m, 3H), 6.97 (ddd, J = 8.2, 7.2, 1.4 Hz, 1H), 6.88 (td, J = 7.4, 1.3 Hz, 1H), 6.73 (ddd, J = 8.2, 7.2, 1.3 Hz, 1H), 6.64 - 6.59 (m, 1H), 6.33 (d, J = 8.4 Hz, 1H), 1.83 (s, 6H), 1.43 (s, 6H). <sup>1</sup>H NMR (125) MHz, DMSO-*d*<sub>6</sub>) δ [ppm]: 139.00, 137.59, 136.14, 135.99, 130.34, 129.55, 127.41, 126.48, 126.12, 123.86, 123.46, 121.29, 120.50, 118.67, 114.70, 112.47, 110.16, 106.78, 35.65, 34.61, 32.56, 28.86. HRMS (ESI): m/z [M+H]<sup>+</sup>, calculated for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>: 341.2007; found: 341.2012.



TMDBP-PM: A mixture of the TMDBP (0.68 g, 2 mmol), 4-(4-bromophenyl)-2,6-diphenylpyrimidine (0.93 g, 2.4 mmol), Pd(OAc)<sub>2</sub> (22.50 mg, 0.1 mmol), t-BuONa (0.38 g, 4 mmol),  $(t-Bu)_3$ PHBF<sub>4</sub> (75.40 mg, 0.26 mmol) and 20 mL dry 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 as a green solid. Yield 72%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ [ppm]: 8.78 (dd, J = 8.0, 1.7 Hz, 2H), 8.55 (d, J = 8.4 Hz, 2H), 8.35 (dd, J = 7.8, 1.9 Hz, 2H),8.12 (s, 1H), 7.64-7.48 (m, 9H), 7.39 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 8.2 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 7.01-6.84 (m, 4H), 6.74 (s, 1H), 6.21-6.15 (m, 1H), 5.91 (d, J = 8.8 Hz)Hz, 1H), 2.12 (s, 6H), 1.54 (s, 6H). <sup>1</sup>H NMR (125 MHz, CDCl<sub>3</sub>) δ [ppm]: 165.16, 164.84, 164.15, 144.49, 138.90, 138.45, 138.21, 138.13, 137.89, 137.53, 137.51, 132.28, 132.15, 130.94, 130.15, 130.04, 129.13, 128.67, 128.65, 127.92, 127.47, 126.68, 126.62, 124.73, 123.55, 123.32, 121.24, 120.16, 113.89, 113.84, 111.73, 110.60, 108.1, 36.33, 34.65, 33.75, 29.29. HRMS (ESI): m/z [M+H]+, calculated for C<sub>46</sub>H<sub>38</sub>N<sub>4</sub>: 647.3169; found: 647.3192.

**TMDBP-TRZ**: It was prepared by the same procedure with TMDBP-TRZ except using 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine as the coupling partner. The product is obtained as a green powder. Yield: 70%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 9.01 (d, *J* = 8.4 Hz, 2H), 8.86 – 8.79 (m, 4H), 7.67 – 7.57 (m, 6H), 7.52 (d, *J* =

8.4 Hz, 3H), 7.38 (dd, J = 7.7, 1.3 Hz, 1H), 7.16 (d, J = 1.5 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.94 – 6.88 (m, 2H), 6.86 (dd, J = 7.8, 1.1 Hz, 1H), 6.73 (s, 1H), 6.16 (d, J = 9.6 Hz, 1H), 5.90 (d, J = 8.8 Hz, 1H), 2.11 (s, 6H), 1.53 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 171.86, 171.11, 145.95, 138.77, 138.24, 138.01, 137.77, 136.09, 132.71, 132.02, 131.90, 131.73, 129.92, 129.04, 128.73, 127.79, 126.55, 126.51, 124.61, 123.43, 123.21, 121.11, 120.05, 113.76, 113.70, 111.60, 108.02, 36.21, 34.54, 33.61, 29.16. HRMS (ESI): m/z [M + H]<sup>+</sup> calculated for C45H37N5: 648.3122; found: 648.3106.





Fig. S2 <sup>13</sup>C NMR spectrum of compound 1.







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. S6** <sup>13</sup>C NMR spectrum of compound TMDBP-PM.





Fig. S8 <sup>13</sup>C NMR spectrum of compound TMDBP-TRZ.



**Fig. S9** TGA traces of TMDBP-PM and TMDBP-TRZ recorded at a heating rate of 10 °C min<sup>-1</sup>. Insert: DSC curves recorded at a heating rate of 10 °C min<sup>-1</sup>.



Fig. S10 The optimal structures of TMDBP-PM and TMDBP-TRZ.

% conformer 
$$i = \frac{\exp\left(-\frac{E_{i}}{k_{b}T}\right)}{\sum_{j} \exp\left(-\frac{E_{j}}{k_{b}T}\right)}$$
 S1

**Equation S1**. The equation of Boltzmann distribution. Where E is the conformational relative energy,  $k_b$  is the Boltzmann constant, and T is the ambient temperature.

Table S1. The two conformers of TMDBP-PM and their potential energies.

TMDBP-PM	QE	QA	
Energy	-1994.89667	-1994.89444	



Fig. S11 Cyclic voltammograms of emitters in dichloromethane for oxidation.



**Fig. S12** UV-vis and fluorescence spectra of TMDBP-PM and TMDBP-TRZ in neat film.



Fig. S13 Fluorescence spectra of TMDBP-based emitters in different solvent

Measured in toluene solutions (10<sup>-5</sup> M) at 298K.



**Fig. S14** The transient photoluminescence decay curves of emitters in doped film under degassed and aerated condition.

Compoun ds	Т <sub>g</sub> [°С]	Τ <sub>d</sub> [°C]	$\lambda_{abs}$ $[nm]^a$	λ <sub>em</sub> [nm] <sup>b</sup>	HOMO/LU MO [eV] <sup>c</sup>	${ m S_1/T_1/}\ \Delta E_{ m ST}{ m d}$	τ <sub>PF</sub> /τ <sub>DF</sub> [ns]/[μs] e	$arPhi_{ m PL}_{ m f}$
TMDBP-	141	361	280 322 394	508	-5 13/-2 40	2 78/2 73/0 05	22/1 59	82
PM			200,522,571	200	5.15/ 2.10	2.10/2.15/0.05	22,1.57	02
TMDBP-	143	360	200 220 412	540	5 12/ 2 52	2 60/2 51/0 06	20/1 29	60
TRZ			280,328,412	540	-3.13/-2.32	2.00/2.54/0.00	50/1.28	09

**Table S2.** The thermos, physical properties and kinetic parameters emitters

<sup>a</sup> Measured in toluene solutions (10<sup>-5</sup> M) at 298K. <sup>b</sup> Measured in the DPEPO films. <sup>c</sup> HOMOs were calculated from CV; LUMO = HOMO +  $E_{g}^{opt}$ . <sup>d</sup> Calculated from the onset wavelengths of the fluorescence (298 K) and phosphorescence (77 K) spectra of both emitters in the DPEPO host. <sup>e</sup> The fitting lifetimes of prompt and DF components and DF ratios of both emitters in toluene solution. <sup>f</sup> PLQY of 10 wt.% both emitters doped into the DPEPO host.



Fig. S15 Chemical structure of the materials used in the devices

 Table S3. Summary of the OLED device data.

Emitters	$V_{on}$ [V] <sup>a</sup>	λ <sub>em</sub> [nm]	PE <sup>b</sup> [lm/W]	CE <sup>b</sup> [cd/A]	EQE <sup>b</sup> [%]	CIE c (x,y)
TMDBP- PM	2.5	510	64.5/51.2/29.3/12.9	71.9/65.4/51.2/32.9	24.2/22.0/17.2/11.1	0.24, 0.53
TMDBP- TRZ	2.5	534	27.8/27.8/24.6/17.7	45.6/35.4/43.0/42.2	13.7/10.7/13.0/12.7	0.36, 0.58

<sup>*a*</sup> Turn-on voltage (at a brightness of 1 cd/m<sup>2</sup>). <sup>*b*</sup> The order of measured value: maximum, then values at the brightness of 100 ,1000 and 5000 cd/m<sup>2</sup>. <sup>*c*</sup> Commission International de l'Eclairage coordinates