Electronic Supplementary Information

Fine-Tuning the Photophysical Properties of Thermally Activated Delayed

Fluorescent Emitters by Torsion Angles: High Performance Sky-blue OLEDs

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General information:

The 400 MHz ¹H and 100 MHz ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500 (400 MHz) in deuterated chloroform with tetramethylsilane (TMS) as an internal reference. High-resolution mass spectrometry (HRMS) spectra was measured by LCQ-Orbitrap Elite (Thermo-Fisher Scientific, Waltham, MA, USA) mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV–2700 spectrophotometer. Photoluminescence (PL) spectra were processed on a Hitachi F-4600 fluorescence spectrophotometer. And the energy levels of S₁ and T₁ are estimated from the onset of the florescence and phosphorescence spectra in the neat film, the delay time is 0.5 ms when the phosphorescence is measured. Differential scanning calorimetry (DSC) from 20 to 350 °C, were measured on a NETZSCH DSC 200 PC unit under argon with a heating rate of 10 °C min⁻¹. The glass transition temperatures (T_g) were calculated out from the second heating scan. Thermo gravimetric analysis (TGA) was recorded on a NEZSCH STA 449C instrument under nitrogen atmosphere at a heating rate of 10 °C/min from 25 °C to 600 °C. The temperature of degradation (T_d) was correlated to a 5% weight. Cyclic voltammetry (CV) was measured on a CHI voltammetric analyzer at room temperature with the conventional threeelectrode configuration, consisted of a platinum column working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo reference electrode. Cyclic voltammograms (CV) were recorded using tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) dissolved in dichloromethane as the supporting electrolyte, and ferrocenium-ferrocene (Fc+/Fc) as the external standard, at the scan rate of 100 mV s⁻¹. The onset potential was calculated out from the intersection of two tangents of the rising and background current in cyclic voltammogram. The PL lifetimes were obtained from a single photon counting spectrometer on Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation light source. Absolute PLQYs were performed with a Quantaurus–QY measurement system (C9920–02, Hamamatsu Photonics), and all the samples were excited at 360 nm.

DFT calculation:

Theoretical simulations were performed using the Gaussian 09 program packages. The geometries were optimized at the B3LYP/def2-SVP level. Time-dependent TD-DFT with PBE0 function and basis set def2-SVP were then performed to further analyze the excited states with the optimized ground state structure. The geometries and FMO distributions were visualized using Gaussview.

Device Fabrication and Measurement:

Indium-tin oxide (ITO) coated glass with a sheet resistance of 15–20 Ω cm⁻² was used as the substrate. Before device fabrication, the ITO glass substrates were cleaned with acetone, detergent,

deionized water, and isopropanol, dried in an oven at 120 °C, and treated with UV-zone for 20 min. After that, the samples were transferred into a deposition system. The devices were fabricated by the multiple source organic molecular beam deposition method in a vacuum at a pressure of 4×10^{-6} mbar. Evaporation rates of 0.4 Å s⁻¹ for the organic materials and 1–4 Å s⁻¹ for the metal electrodes were applied. The thickness of each deposition layer was monitored using a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). The EL spectra were recorded on a PR735 fluorescence spectrophotometer. The current density–voltage–luminance (J–V–L) characteristics were recorded simultaneously by using a computer-controlled source meter (Keithley 2400) equipped with a light intensity meter LS-110 under an ambient atmosphere without encapsulation. The EQEs were calculated from the luminance, current density and EL spectrum, assuming a Lambertian distribution. All the results of the devices were measured in the forward-viewing direction without any out-coupling enhancement techniques.

X-Ray Structural Analysis:

Single crystal **2,3**'**ACSO2** and **2,4**'**ACSO2** are obtained from slow evaporation of nhexane/CH₂Cl₂ solution at room temperature. Single-crystal X-ray-diffraction data were obtained from a Super Nova, Dual, Cu at zero, AtlasS2 diffractometer through using MoK α ($\lambda = 0.71073$), CuK α ($\lambda = 1.54184$ Å) with a *w*/2 θ scan mode at the temperature of 100 K. Structure of the crystal was solved by direct methods using the SHELXS-97 software. None-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F² using SHELXL-97, while the hydrogen atoms were directly introduced at calculated position and refined in the riding mode. Drawings were produced using Ortep 3 and Mercury 3.3. CCDC-1917434 (**2,3**'**ACSO**₂) and CCDC-1917432 (**2,4'ACSO**₂) contain supplementary crystallographic data. The data can be obtained free

Sample	2,3'ACSO ₂	2,4'ACSO ₂	
Empirical formula	$C_{42}H_{36}N_2O_2S$	$C_{42}H_{36}N_2O_2S$	
CCDC No.	1917434	1917432	
Formula weight	632.79	632.79	
Temperature/K	100.01(10)	100.00(10)	
Crystal system	orthorhombic	triclinic	
Space group	$P2_{1}2_{1}2_{1}$	P-1	
a/Å	8.5922(8)	12.9444(6)	
b/Å	16.4651(18)	12.9605(6)	
c/Å	23.2456(18)	20.6567(10)	
α/°	90	88.355(4)	
β/°	90	89.920(4)	
γ/°	90	86.340(4)	
Volume/Å ³	3288.6(5)	3457.0(3)	
Z	4	4	
$\rho_{calc}g/cm^3$	1.278	1.216	
μ/mm^{-1}	0.139	1.125	
F(000)	1336.0	1336.0	
Crystal size/mm ³	$0.14 \times 0.11 \times 0.1$	$0.11 \times 0.1 \times 0.08$	
Radiation	MoK α ($\lambda = 0.71073$)	$CuK\alpha (\lambda = 1.54184)$	
2Θ range for data collection/°	4.29 to 49.988	4.28 to 147.872	
Inday non ooo	$-10 \le h \le 8, -19 \le k \le 13, -27$	$-16 \le h \le 15, -15 \le k \le 15, -$	
index ranges	$\leq l \leq 27$	$25 \le l \le 23$	
Reflections collected	10775	25004	
Indonondont reflections	5746 [$R_{int} = 0.0699$, $R_{sigma} =$	13535 [$R_{int} = 0.0387$, $R_{sigma} =$	
independent reflections	0.1142]	0.0517]	
Data/restraints/parameters	5746/0/428	13535/0/855	
Goodness-of-fit on F ²	1.003	1.045	
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0605, wR_2 = 0.1156$	$R_1 = 0.0439, wR_2 = 0.1130$	
Final R indexes [all data]	$R_1 = 0.0810, wR_2 = 0.1298$	$R_1 = 0.0525, wR_2 = 0.1194$	
Largest diff. peak/hole / e Å-3	0.27/-0.32	0.29/-0.56	

Table S2. Crystal data and structure refinements for 2,3'ACSO₂ and 2,4'ACSO₂.

Synthesis and characterization:

Synthetic routes:



Scheme S1. Synthetic routes of x-ACSO₂.

The key intermediates, 1-fluoro-2-((4-fluorophenyl)sulfonyl)benzene (M3) and 1-bromo-3-((4-bromophenyl)sulfonyl)benzene (M4) were synthesized according to the literatures. Standard procedures are used to dry the solvents. And all reagents were used as received without further purification, unless otherwise stated.

Synthesis of 1-((3-bromophenyl)sulfonyl)-2-fluorobenzene (M1):

A mixture of 2-fluorobenzenthiol (0.64 g, 5 mmol), 1-Bromo-3-iodobenzene, (1.7 g, 6 mmol), bis(dibenzylideneaceton)palladium (144 mg, 0.25 mmol), Bis(2-diphenylphosphinophenl)ether (405 mg, 0.75 mmol) and sodium tert-butoxide (0.74 g, 7.5 mmol) and 50 mL redistilled toluene was purged with argon and then heated to 110 °C and stirred for 48 h. After cooling to room temperature, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was then added with 20 mL 30% hydrogen peroxide and 20 mL acetic acid and then heated to 130 °C and stirred for 48 h. After cooling to room

temperature, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (4:1 by vol.) as eluent to afford a white powder. (0.94 g, 60% yield) ¹H NMR (400 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 8.16 – 8.05 (m, 2H), 7.96 (dq, *J* = 7.9, 1.4 Hz, 1H), 7.74 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.35 (td, *J* = 7.7, 1.1 Hz, 1H), 7.14 (ddd, *J* = 9.7, 8.3, 1.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 160.48, 157.93, 142.65, 136.82, 136.55, 136.47, 130.99, 130.97, 130.75, 129.85, 128.79, 128.65, 126.82, 126.80, 124.89, 124.85, 123.02, 117.56, 117.35. HRMS (ESI) m/z calcd for C₁₂H₉BrFO₂S⁺ (M+H)⁺ 314.94852, found 314.94882.

Synthesis of 10-(3-((2-fluorophenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (**M2**): A mixture of M1 (0.94 g, 3 mmol), 9,9-dimethyl-9,10-dihydroacridine (1.5 g, 7 mmol), palladium acetate (34 mg, 0.15 mmol), tri-tert-butylphosphine tetrafluoroborate (135 mg, 0.45 mmol), sodium tert-butoxide (672 mg, 7 mmol) and 50 mL redistilled toluene was purged with argon and then heated to 110 °C and stirred for 48 h. After cooling to room temperature, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1 by vol.) as eluent to afford a white powder. (1.0 g, 80% yield) ¹H NMR (400 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 8.16 – 8.09 (m, 2H), 8.05 (q, *J* = 1.7 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.51 – 7.43 (m, 2H), 7.34 (td, *J* = 7.7, 1.1 Hz, 1H), 7.16 (ddd, *J* = 9.6, 8.3, 1.1 Hz, 1H), 7.00 – 6.91 (m, 4H), 6.17 – 6.08 (m, 2H), 1.68 (s, 6H). ¹³C NMR (100 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 160.53, 157.97, 143.73, 142.22, 140.42, 137.27, 136.42, 136.33, 131.85, 131.56, 131.54, 130.39, 129.87, 129.13, 128.99, 127.87, 127.85, 126.50, 125.41, 124.88, 124.84, 121.22, 117.50, 117.29, 113.88, 36.04, 31.07. HRMS (ESI) m/z calcd for C₂₇H₂₃FNO₂S⁺ (M+H)⁺ 444.14280, found 444.14270.

Synthesis of 10-(2-((3-(9,9-dimethylacridin-10(9H)-yl)phenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (**2,3'ACSO**₂):

A mixture of sodium hydride (70 wt.% in oil dispersion, 0.12 g, 3.5 mmol) and 9,9-dimethyl-9,10dihydroacridine (0.73 g, 3.5 mmol) in dry THF (20 mL) was heated to 60 °C and stirred for 30 min under argon. And then M2 (1.0 g, 2.2 mmol) was added to the reaction mixture in one portion. After heating at 60 °C for 24 h, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was purified by column chromatography on silica gel using petroleum ether /dichloromethane (1:1 by vol.) as eluent to afford a white powder. (1.6 g, 86% yield) ¹H NMR (400 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 8.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 (td, *J* = 7.6, 1.6 Hz, 1H), 7.78 – 7.66 (m, 3H), 7.48 – 7.40 (m, 4H), 7.31 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.94 (dd, *J* = 6.0, 3.3 Hz, 4H), 6.87 (td, *J* = 7.5, 1.3 Hz, 2H), 6.76 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 2H), 5.97 (dd, *J* = 6.0, 3.4 Hz, 2H), 5.68 (dd, *J* = 8.2, 1.2 Hz, 2H), 1.85 (s, 3H), 1.64 (d, *J* = 4.8 Hz, 9H). ¹³C NMR (100 MHz, CDCl3, 25 °C) δ [ppm]: 142.69, 141.64, 141.62, 141.58, 140.44, 140.03, 136.96, 136.60, 134.71, 132.03, 130.91, 130.63, 130.37, 129.76, 129.65, 128.29, 126.40, 126.38, 126.25, 125.21, 121.16, 121.03, 114.62, 113.96, 36.33, 36.01, 35.70, 31.46, 30.76. HRMS (ESI) m/z calcd for $C_{42}H_{37}N_2O_2S^+$ (M+H)⁺ 633.25703, found 633.25714.

Synthesis of 10-(2-((4-(9,9-dimethylacridin-10(9H)-yl)phenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (2,4'ACSO₂):

A mixture of sodium hydride (70 wt.% in oil dispersion, 0.24 g, 7 mmol) and 9,9-dimethyl-9,10dihydroacridine (1.5 g, 7 mmol) in dry THF (20 mL) was heated to 60 °C and stirred for 30 min under argon. And then M3 (0.76 g, 3 mmol) was added to the reaction mixture in one portion. After heating at 60 °C for 24 h, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was purified by column chromatography on silica gel using petroleum ether /dichloromethane (1:1 by vol.) as eluent to afford a light-yellow powder (1.5 g, 80% yield) ¹H NMR ((400 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 8.66 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.95 – 7.76 (m, 4H), 7.44 (ddd, *J* = 7.1, 5.5, 1.8 Hz, 4H), 7.34 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.98 (td, *J* = 7.0, 1.8 Hz, 4H), 6.92 – 6.77 (m, 4H), 1.88 (s, 3H), 1.64 (d, *J* = 13.4 Hz, 9H). ¹³C NMR (100 MHz, CDCl3, 25 °C) δ [ppm]: 146.08, 141.93, 141.53, 140.15, 140.11, 138.91, 136.94, 134.78, 132.09, 131.37, 130.73, 130.01, 129.70, 129.67, 126.35, 126.26, 126.04, 125.28, 121.51, 121.22, 115.15, 114.95, 36.46, 36.13, 35.72, 30.89, 30.85. HRMS (ESI) m/z calcd for C₄₂H₃₇N₂O₂S⁺ (M+H)⁺ 633.25703, found 633.25745.

Synthesis of 10-(3-((4-(9,9-dimethylacridin-10(9H)-yl)phenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (**3,4'ACSO**₂): A mixture of M4 (1.13 g, 3 mmol), 9,9-dimethyl-9,10-dihydroacridine (1.5 g, 7 mmol), palladium acetate (34 mg, 0.15 mmol), tri-tert-butylphosphine tetrafluoroborate (135 mg, 0.45 mmol), sodium tert-butoxide (672 mg, 7 mmol) and 50 mL redistilled toluene was purged with argon and then heated to 110 °C and stirred for 48 h. After cooling to room temperature, the reaction mixture was treated with brine and then extracted with dichloromethane for three times. The organic layers were collected and combined. Then, the solvent was removed by using rotary evaporators. The resulting product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1 by vol.) as eluent to afford a white powder. (1.5 g, 78% yield) ¹H NMR (400 MHz, CDCl₃ + TMS, 25 °C) δ [ppm]: 8.24 – 8.12 (m, 3H), 8.04 (t, J = 1.9 Hz, 1H), 7.85 (t, J = 7.9 Hz, 1H), 7.64 (ddd, J = 7.8, 2.0, 1.1 Hz, 1H), 7.56 - 7.43 (m, 6H), 7.02 - 6.89 (m, 8H), 6.31 -6.23 (m, 2H), 6.17 - 6.08 (m, 2H), 1.67 (d, J = 16.6 Hz, 12H). ¹³C NMR (100 MHz, CDCl3, 25) °C) δ [ppm]:146.85, 144.30, 142.62, 140.41, 140.21, 139.84, 137.04, 132.22, 131.85, 131.17, 130.76, 130.49, 130.46, 127.48, 126.55, 126.50, 125.55, 125.44, 121.83, 121.35, 115.10, 113.82, 36.27, 36.08, 31.15, 30.76. HRMS (ESI) m/z calcd for $C_{42}H_{37}N_2O_2S^+$ (M+H)⁺ 633.25703, found 633.25751.



Figure S1. ¹H NMR spectra of M1.



Figure S2. ¹³C NMR spectra of M1.



Figure S3. ¹H NMR spectra of M2.



Figure S4. ¹³C NMR spectra of M2.



Figure S5. ¹H NMR spectra of 2,3'ACSO₂.



Figure S6. ¹³C NMR spectra of **2,3'ACSO**₂.



Figure S7. ¹H NMR spectra of 2,4'ACSO₂.



Figure S8. ¹³C NMR spectra of 2,4'ACSO₂.



Figure S9. ¹H NMR spectra of 3,4'ACSO₂.



Figure S10. ¹³C NMR spectra of **3,4'ACSO**₂.

ZLS-1. HRMS (ESI) m/z calcd for C₄₂H₃₇N₂O₂S⁺ (M+H)⁺ 633.25703, found 633.25714.



Figure S11. High-resolution mass data of 2,3'ACSO₂.





Figure S12. High-resolution mass data of 2,4'ACSO₂.



ZLS-3. HRMS (ESI) m/z calcd for C₄₂H₃₇N₂O₂S⁺ (M+H)⁺ 633.25703, found 633.25751.

Figure S13. High-resolution mass data of 3,4'ACSO₂.



Figure S14. The transient PL spectra of (a) 2,3'ACSO₂, (b) 2,4'ACSO₂ and (c) 3,4'ACSO₂

doped into DPEPO films (10 wt%) from 100 to 300 K.

 $k_{\rm p}^{\rm d)}$ $k_{d}^{d)}$ k_{nr}e) k_{ISC}^{e)} $k_{\rm RISC}^{e)}$ $au_{p}{}^{a)}$ $\tau_d{}^{a)}$ $\Phi_{PL}{}^{b)}$ Φ_p^{c)} $\Phi_d^{c)}$ Compounds (×107 s-(×10⁵ s⁻ (×107 s-(×10⁵ s⁻ (×10⁷ s⁻ $k_{\rm p}/k_{\rm nr}$ [ns] [%] [%] [%] [µs] 1) 1) 1) 1) 1) 2,3'ACSO₂ 26 3.1 59 38 21 3.8 3.2 1.3 5.0 1.0 3.8 2,4'ACSO2 7.9 23 3.3 42 4.3 3.0 2.8 8.4 0.5 65 23 3,4'ACSO2 17 4.4 77 44 5.9 2.3 3.4 5.3 0.6 33 10.0

 Table S2. Photoluminescence properties of x-ACSO2 doped into DPEPO (10 wt%) films at room

 temperature.

a) The lifetimes of prompt and delayed fluorescence. b) The total fluorescence PLQY under oxygenfree conditions. c) The prompt and delayed fluorescence PLQY under oxygen-free conditions. d) The rate constants of prompt and delayed radiative. e) The rate constants of ISC, RISC and nonradiation transition process.



Figure S15. Current efficiency and power efficiency versus current density curves.

Device	dopant	Voltage ^{a)}	FOF ^{b)} (%)	CF ^{b)} (cd/A)	PE ^{b)} (lm/W)	Roll-off ^{c)} (%)
		(V)	LQL (/0)			
А	2,3'ACSO ₂	3.5	13.0/6.5/-	34.1/17.1/-	30.6/10.8/-	50.0/100
В	2,4'ACSO ₂	3.5	12.8/6.7/-	31.9/16.8/-	28.4/11.2/-	47.7/100
С	3,4'ACSO ₂	3.0	20.5/18.5/13.2	40.7/36.3/26.1	36.3/25.5/12.0	9.8/36

Table S3. Summary of the EL data of devices at different luminance.

a) The turn-on voltage recorded at a brightness of 1 cd m⁻²; b) Maximum value, values at 100 and 1000 cd m⁻²; c) The external quantum efficiency roll-off at 100 and 100 cd m⁻².



Figure S16. The optimized structures and HOMO/LUMO distributions of DMAC-DPS.

compound	calculated	Calculated	Calculated	calculated $E_{\rm g}$
	$E_{\rm S1}/E_{\rm T1} [{\rm eV}]$	$\Delta E_{\rm ST}$ [eV]	HOMO/LUMO [eV]	[eV]
DMAC-DPS	3.003/2.985	0.018	-5.492/-2.050	3.442

Table S4. The theoretical data of DMAC-DPS obtained from TD-DFT calculation.



Figure S17. (a) EL spectra of the device based on DMAC-DPS; (b) PE/CE/EQE versus current density curves.

Reference:

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- [3] W. Zeng, S. Gong, C. Zhong and C. Yang, J. Phys. Chem. C, 2019, 123, 10081-10086.