

Electronic Supplementary Information (ESI)

High-performance blue organic light-emitting diodes with 20% external electroluminescence quantum efficiency based on pyrimidine-containing thermally activated delayed fluorescence emitters

In Seob Park,^{ab} Jiyoung Lee^a and Takuma Yasuda^{*ab}

^a INAMORI Frontier Research Center (IFRC), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

^b Department of Applied Chemistry, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

* E-mail: yasuda@ifrc.kyushu-u.ac.jp

Table of Contents:

General methods.	S2
Synthesis and characterization.	S4
Determination of rate constants.	S6
Table S1. TD-DFT calculation results	S7
Table S2. Rate constants and quantum efficiencies	S7
Figure S1. Fluorescence and phosphorescence spectra	S8
Figure S2. EL spectra of TADF-OLEDs at different voltages	S8
References	S8

General methods. All reagents and solvents were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Wako Pure Chemical Industries, and used as received unless otherwise noted. Methyl-2-(phenylamino)benzoate,¹ 9-phenyl-9*H*-3,9'-bicarbazole (CCP),² and 2,8-bis(diphenylphosphine oxide)dibenzofuran (PPF)³ were prepared according to previously reported procedures, and were further purified by temperature-gradient vacuum sublimation. 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) was donated by the Nippon Soda Corporation, and was then purified by vacuum sublimation before use. Other OLED materials were purchased from E-Ray Optoelectronics Technology Corporation, and used for device fabrication without further purification. NMR spectra were recorded on Bruker Avance III 400 and 500 spectrometers. Chemical shifts of ¹H and ¹³C NMR signals were referenced to tetramethylsilane (δ = 0.00), CDCl₃ (δ = 77.0), and DMSO-*d*₆ (δ = 39.5) as internal standards, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were performed using a Yanaco MT-5 CHN coder.

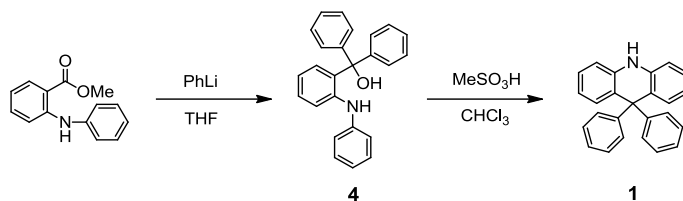
Quantum chemical calculations. Density functional theory (DFT) calculations for the pyrimidine-based molecules were performed using the Gaussian 09 program package. Geometries in the ground state were optimized using the PBE1PBE functional with the 6-31G(d) basis set in the gas phase. The lowest singlet and triplet excited states were computed using the optimized structures with time-dependent DFT (TD-DFT) at the same level. The PBE1PBE/6-31G(d) method can provide a better correlation with the experimental ΔE_{ST} than the standard B3LYP/6-31G(d) method, without increasing the computational time.

Photophysical characterizations. Organic thin films for photophysical measurements were prepared by vacuum deposition under high vacuum ($\sim 7 \times 10^{-5}$ Pa) onto a quartz glass or Si(100) substrate. UV/vis absorption and photoluminescence (PL) spectra were measured using a Jasco V-670 spectrometer and a Jasco FP-8600 spectrophotometer, respectively, using degassed spectral grade solvents. The absolute PL quantum yields (Φ_{PL}) were measured using a Jasco ILF-835 integrating sphere system. The transient PL characteristics of the doped thin films were performed using a Quantaaurus-Tau C11367 (λ_{ex} = 340 nm, pulse width = 100 ps, repetition rate = 20 Hz) under N₂ atmosphere, and a Hamamatsu Photonics C9300 streak camera with a N₂ gas laser (λ_{ex} = 337 nm, pulse width = 500 ps, and repetition rate = 20 Hz) under vacuum ($< 4 \times 10^{-1}$ Pa). The HOMO energy levels of the materials in the thin films were determined

using a Riken-Keiki AC-2 ultraviolet photoelectron spectrometer. The LUMO energy levels were estimated by subtracting the optical energy gap (E_g) from the measured HOMO energies; E_g values were determined from the high energy onset position of the PL spectra of the thin films.

OLED fabrication and measurements. Indium tin oxide (ITO)-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropanol, and then subjected to UV-ozone treatment for 30 min, before loading into a vacuum evaporation system. The organic layers and a cathode aluminum layer were thermally evaporated through shadow masks under vacuum ($< 6 \times 10^{-5}$ Pa) with an evaporation rate of $< 0.3 \text{ nm s}^{-1}$. The layer thickness and deposition rates were monitored in situ during deposition by an oscillating quartz thickness monitor. OLED properties were measured using a Keithley 2400 source meter and a Konica Minolta CS-2000 spectroradiometer.

Synthesis and characterization.



Scheme S1. Synthesis of 9,9-diphenyl-9,10-dihydroacridine (**1**).

Synthesis of 9,9-diphenyl-9,10-dihydroacridine (1**):** To a solution of methyl-2-(phenylamino)benzoate¹ (18.0 g, 79.2 mmol) in dry THF (300 mL) was added dropwise phenyllithium (1.6 M, 148.5 mL, 237.6 mmol) at $-78\text{ }^{\circ}\text{C}$ under N_2 . The mixture was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$, and then further reacted for 2 h at $0\text{ }^{\circ}\text{C}$. After heating up to room temperature, the mixture was reacted for 4 h at room temperature, and then quenched by addition of a large amount of water. The product was extracted with chloroform and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the crude product was used in the next reaction without further purification.

To a solution of **4** in chloroform (300 mL) was added methanesulfonic acid (8.4 g, 87.1 mmol) at room temperature. The mixture was refluxed for 1 h under air, and then further reacted for 12 h at room temperature. The reaction mixture was concentrated under reduced pressure. Then, the residue was purified by column chromatography on silica gel (hexane/chloroform = 3:1, v/v) to give **1** as a white solid (yield = 18.5 g, 70%). ¹H NMR (500 MHz, CDCl_3): δ 7.26-7.19 (m, 4H), 7.17-7.16 (m, 4H), 6.96-6.94 (m, 4H), 6.90-6.87 (m, 2H), 6.83 (dd, J = 7.8 Hz, 1.5 Hz, 2H), 6.80 (dd, J = 7.9 Hz, 1.1 Hz, 2H), 6.28 (s, 1H); MS (MALDI-TOF) m/z [M]⁺ calcd 333.15; found, 333.97.

Synthesis of 10-(4-bromophenyl)-9,9-diphenyl-9,10-dihydroacridine (2**):** A solution of **1** (15.0 g, 44.9 mmol) in 1,4-dioxane (150 mL) was added slowly sodium *tert*-butoxide (8.6 g, 89.8 mmol) at room temperature under N_2 . After stirred for 30 min, copper (I) iodide (0.85 g, 4.5 mmol), 1,10-phenanthroline (0.81 g, 4.5 mmol), and 4-bromoiodobenzene (15.2 g, 53.9 mmol) were added to the reaction mixture. The mixture was refluxed for 12 h. After cooling to room temperature, water (ca. 150 mL) was added to the reaction mixture. After filtered through a Celite pad, the product was extracted with chloroform and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the product was purified by column chromatography on silica gel (hexane/chloroform = 10:1, v/v) to give **2** as a white solid (yield = 18.6 g, 85%). ¹H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.84-7.80 (m, 2H), 7.34-7.30 (m, 6H), 7.12-7.08 (m, 2H), 7.04-7.01 (m, 2H), 6.94-6.88 (m, 6H), 6.77 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 6.34 (dd, J = 8.3 Hz, 1.0 Hz, 2H); MS

(MALDI-TOF) m/z : $[M+H]^+$ calcd 487.09; found, 487.18.

Synthesis of 9,9-diphenyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridine (3): To a solution of **2** (5.0 g, 10.2 mmol) in dry THF (400 mL) was added dropwise *n*-butyllithium (2.6 M, 4.7 mL, 12.3 mmol) at $-78\text{ }^{\circ}\text{C}$ under N_2 . The mixture was stirred for 1 h at that temperature. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.3 g, 12.3 mmol) was added dropwise to the mixture at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was further stirred for 3 h at room temperature. The resulting mixture was added into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) to afford **3** as a white solid (yield = 4.0 g, 73%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.92 (d, J = 8.0 Hz, 2H), 7.35-7.25 (m, 6H), 7.11-7.04 (m, 4H), 6.92-6.88 (m, 6H), 6.77 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 6.29 (dd, J = 6.8 Hz, 0.8 Hz, 2H), 1.33 (s, 12H); MS (MALDI-TOF) m/z : $[M]^+$ calcd 535.27; found, 535.88.

Synthesis of 2DPAc-MPM: A mixture of **3** (2.00 g, 3.74 mmol), 4,6-dichloro-2-methylpyrimidine (0.24 g, 1.47 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.13 g, 0.11 mmol) in dry toluene (80 mL) was stirred under N_2 . An aqueous solution (30 mL) of potassium carbonate (1.55 g, 11.22 mmol) was added to the mixture, which was refluxed for 48 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad. After extracting with chloroform and drying over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate/chloroform = 10:1:3, v/v/v) to give 2DPAc-MPM as a light-yellow solid (yield = 1.94 g, 57%). This compound was further purified by temperature-gradient sublimation under vacuum. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.60 (d, J = 8.0 Hz, 5H), 7.37-7.25 (m, 16H), 7.12 (t, J = 7.2 Hz, 4H), 6.95-6.92 (m, 12H), 6.80 (d, J = 6.8 Hz, 4H), 6.44 (d, J = 8.4 Hz, 4H), 2.81 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , δ): 168.95, 164.33, 146.38, 143.31, 141.94, 137.26, 131.95, 130.39, 130.14, 129.71, 129.52, 127.65, 126.88, 126.30, 120.40, 114.08, 110.35, 56.76, 26.54; MS (MALDI-TOF) m/z : $[M+H]^+$ calcd 909.40; found, 909.65. Anal. calcd for $\text{C}_{67}\text{H}_{48}\text{N}_4$: C 88.52, H 5.32, N 6.16; found: C 88.35, H 5.12, N 6.16.

Synthesis of 2DPAc-PPM: This compound was synthesized according to the same procedure as described above for the synthesis of 2DPAc-MPM, except that fenclorim (0.34 g, 1.5 mmol) was used as the reactant instead of 4,6-dichloro-2-methylpyrimidine. 2DPAc-PPM was obtained as a light-yellow solid (yield = 2.36 g, 65%), and was further

purified by temperature-gradient sublimation under vacuum. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.77 (d, $J = 8.4$ Hz, 4H), 8.74-8.71 (m, 3H), 7.64-7.61 (m, 3H), 7.38-7.28 (m, 16H), 7.13 (t, $J = 8.0$ Hz, 4H), 6.96-6.93 (m, 12H), 6.81 (d, $J = 8.0$ Hz, 4H), 6.48 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3 , δ): 164.22, 146.38, 143.42, 141.96, 137.81, 137.25, 131.90, 130.95, 130.41, 130.13, 129.79, 129.53, 128.58, 128.50, 127.67, 126.93, 126.32, 120.42, 114.10, 110.54, 56.79, 30.94; MS (MALDI-TOF) m/z : $[M+H]^+$ calcd 971.41; found, 971.51. Anal. calcd for $\text{C}_{72}\text{H}_{50}\text{N}_4$: C 89.04, H 5.19, N 5.77; found: C 89.13, H 5.09, N 5.84.

Determination of rate constants. The PL quantum efficiencies of the prompt component (Φ_p) and delayed component (Φ_d) are experimentally obtained from the emission intensity proportions of their components in the transient PL. The lifetimes of the prompt component (τ_p) and delayed component (τ_d) are determined by fitting the transient PL decay curve. In the presence of intersystem crossing (ISC) and reverse intersystem crossing (RISC) between the S_1 and T_1 states, the rate constants of the prompt component (k_p) and delayed component (k_d) can be expressed by the following formulas:

$$k_p = \frac{1}{\tau_p} = k_r^S + k_{nr}^S + k_{ISC} \quad (1)$$

$$k_d = \frac{1}{\tau_d} = k_{nr}^T + \left(1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}}\right) k_{RISC} \quad (2)$$

where k_r^S and k_{nr}^S are the radiative and non-radiative decay rate constants of the S_1 state, respectively, and k_{ISC} and k_{RISC} are the ISC ($S_1 \rightarrow T_1$) and RISC ($T_1 \rightarrow S_1$) rate constants, respectively. k_r^S and k_{ISC} are assumed to be much faster than k_{nr}^T and k_{RISC} . The Φ_p , Φ_d , and Φ_{ISC} are given by the following formulas:

$$\Phi_p = \frac{k_r^S}{k_r^S + k_{nr}^S + k_{ISC}} = \frac{k_r^S}{k_p} \quad (3)$$

$$\Phi_d = \sum_{k=1}^{\infty} (\Phi_{ISC} \Phi_{RISC})^k \Phi_p = \frac{\Phi_{ISC} \Phi_{RISC}}{1 - \Phi_{ISC} \Phi_{RISC}} \cdot \Phi_p \quad (4)$$

$$\Phi_{ISC} = \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} = \frac{k_{ISC}}{k_p} \quad (5)$$

From Eqs. 1–5, the following equation can be obtained.

$$k_{RISC} = \frac{k_p k_d}{k_{ISC}} \frac{\Phi_d}{\Phi_p} \quad (6)$$

Since the Φ_p exhibits almost negligible temperature dependence, we assume that $k_{nr}^S \approx 0$ at 300 K. Based on Eqs. 1–6, k_r^S , k_{ISC} , and k_{RISC} can be estimated, as listed in **Table S2**.

Table S1. TD-DFT calculation results. The lowest excited singlet (S_1) and triplet (T_1) energies, oscillator strength (f), and transition configurations of the pyrimidine derivatives calculated at the PBE1PBE/6-31G(d) level.

compound	state	E (eV)	f	main configuration		ΔE_{ST} (eV)
2DPAC-MPM	S_1	2.62	0.0002	H $\rightarrow$ L	0.693	0.16
	T_1	2.46	0	H-1 $\rightarrow$ L	0.557	
				H-5 $\rightarrow$ L	0.290	
2DPAC-PPM	S_1	2.60	0.0010	H $\rightarrow$ L	-0.694	0.15
	T_1	2.45	0	H-1 $\rightarrow$ L	0.559	
				H-3 $\rightarrow$ L	-0.235	

H $\rightarrow$ L represents the HOMO to LUMO transition. Excitation configurations with the highest contributions are presented, together with the corresponding transition symmetry and nature of the involved orbitals.

Table S2. Rate constants and quantum efficiencies of the pyrimidine derivatives in doped thin films.^a

compound	k_r^S [s ⁻¹]	k_d [s ⁻¹]	k_{ISC} [s ⁻¹]	k_{RISC} [s ⁻¹]	Φ_p [%]	Φ_d [%]	Φ_{ISC} [%]	Φ_{RISC} [%]
2DPAC-MPM	4.4×10^6	2.1×10^3	1.6×10^7	8.7×10^3	22	70	78	90
2DPAC-PPM	1.8×10^6	3.8×10^3	1.1×10^7	2.5×10^4	14	80	86	93

^aAbbreviations: k_r^S , radiative rate constant ($S_1 \rightarrow S_0$); k_d , delayed-radiative rate constant ($S_1 \rightarrow T_1 \rightarrow S_1 \rightarrow S_0$); k_{ISC} , intersystem-crossing (ISC) rate constant ($S_1 \rightarrow T_1$); k_{RISC} , reverse ISC rate constant ($T_1 \rightarrow S_1$); Φ_p , quantum efficiency for prompt fluorescence component; Φ_d , quantum efficiency for delayed fluorescence component; Φ_{ISC} , ISC quantum efficiency; Φ_{RISC} , RISC quantum efficiency.

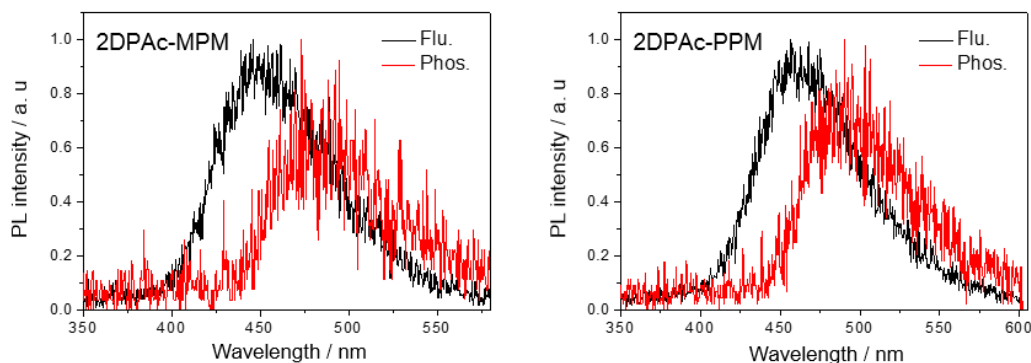


Figure S1. PL spectra of prompt fluorescence in the range of 1–100 ns at 300 K (black) and phosphorescence at 5 K in the range of 100–10000 μ s (red) for 2DPAc-MPM:PPF (left) and 2DPAc-PPM:PPF (right) doped thin films. The lowest excited singlet (S_1) and triplet energy (T_1) levels of the TADF emitters were estimated from the high energy onsets of the fluorescence and phosphorescence spectra, respectively.

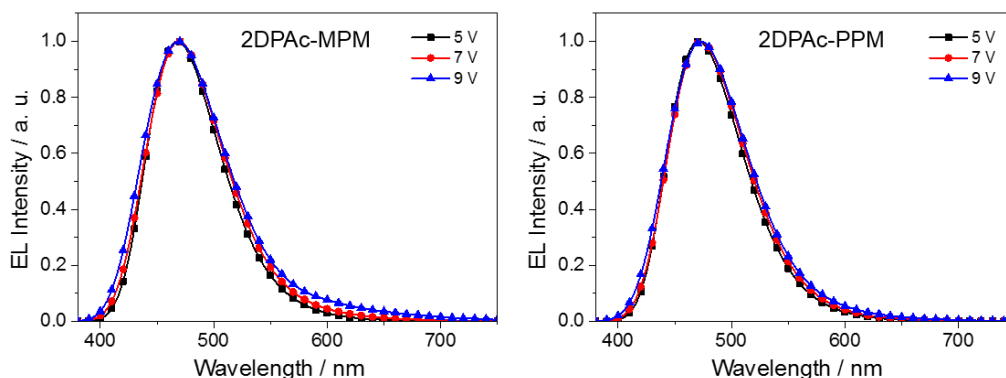


Figure S2. Normalized EL spectra of blue TADF-OLEDs based on 2DPAc-MPM (left) and 2DPAc-PPM (right) taken at different voltages.

References

- 1 T. Takahashi, K. Shizu, T. Yasuda, K. Togashi and C. Adachi, *Sci. Technol. Adv. Mater.*, 2014, **15**, 034202.
- 2 M. Numata, T. Yasuda and C. Adachi, *Chem. Commun.*, 2015, **51**, 9443.
- 3 P. A. Vecchi, A. B. Padmaperuma, H. Qiao, L. S. Sapochak and P. E. Burrows, *Org. Lett.*, 2006, **8**, 4211.