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Supporting information

Light-Blue Thermally Activated Delayed Fluorescent Emitters Realizing a High External Quantum Efficiency of 25% and Unprecedented Low Drive Voltages in OLEDs

Ryutaro Komatsu,[a] *Hisahiro Sasabe,**[a,b] *Yuki Seino,*[a] *Kohei Nakao,*[a] *and Junji Kido**[a,b]

a. Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata, 992-8510 Japan.
b. Research Center for Organic Electronics (ROEL), Yamagata University, Yonezawa, Yamagata, 992-8510 Japan.

E-mail: h-sasabe@yz.yamagata-u.ac.jp; kid@yz.yamagata-u.ac.jp

General procedure

General Considerations: Quantum chemical calculations were performed using the hybrid DFT functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages. Electrons were described by the Pople's 6-31G(d) and 6-311+G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL 400 (400 MHz) spectrometer. Mass spectrum was obtained using a JEOL JMS-K9 mass spectrometer. DSC was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. TGA was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. UV–vis spectra was measured using a Shimadzu UV-3150 UV–vis–NIR spectrophotometer. Photoluminescence spectra were measured using a FluoroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The I_p was determined by a PYS under the vacuum (=10^{-3} Pa). Transient PL decay curves and time resolved photoluminescence spectra were measured by using a streak camera (C4334 from Hamamatsu Photonics) at 5 K and 300 K.

Device Fabrication and Characterization: The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 minutes by exposure to UV–ozone. The organic layers were deposited onto the ITO substrates under the vacuum (=10^{-5} Pa), successively. LiF and Al was patterned using a shadow mask with an array of 2 mm × 2mm openings without breaking the vacuum (=10^{-5} Pa). The electroluminescent (EL) were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured by using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

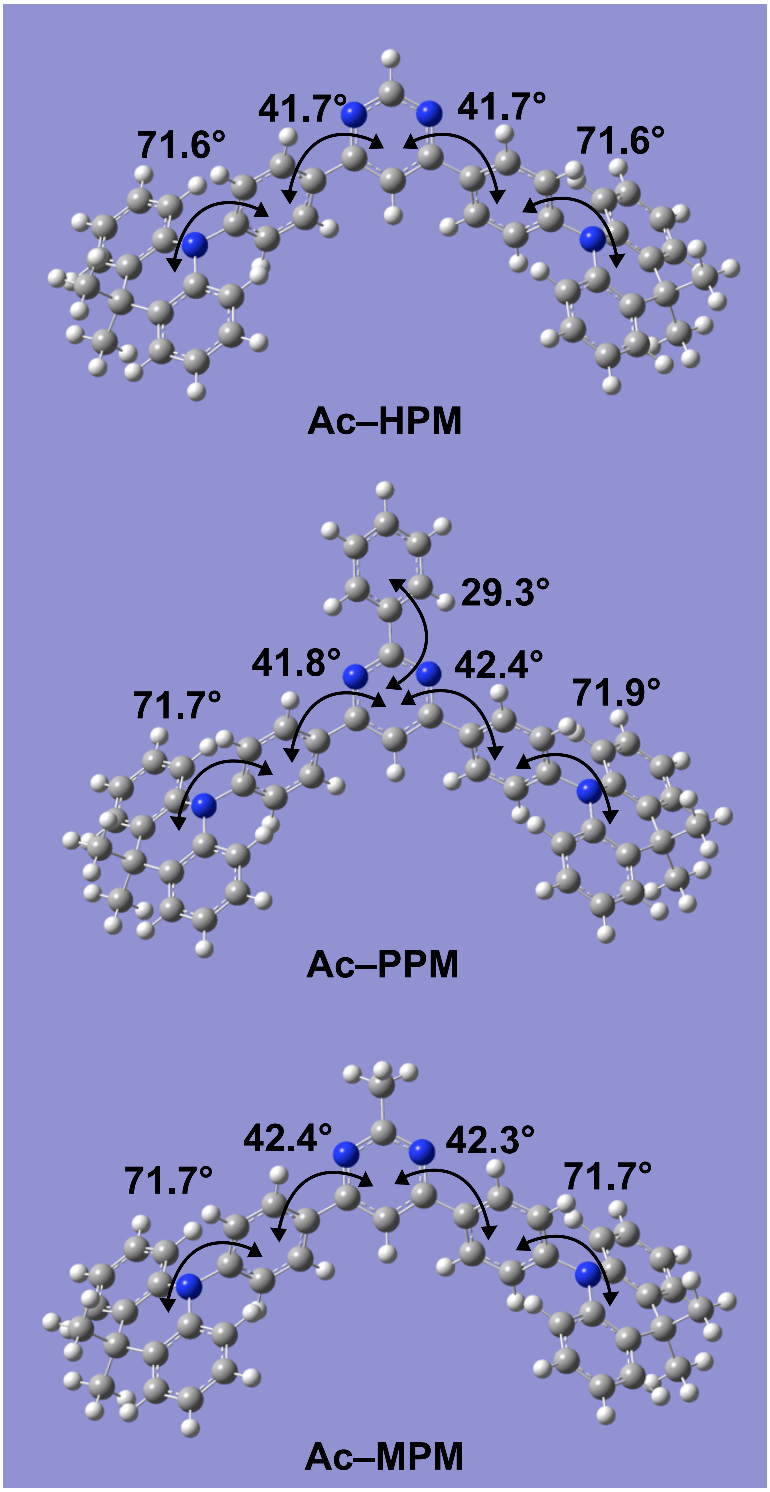


Figure S-1. Optimized molecular structures and dihedral angles of **Ac–RPM** derivatives.

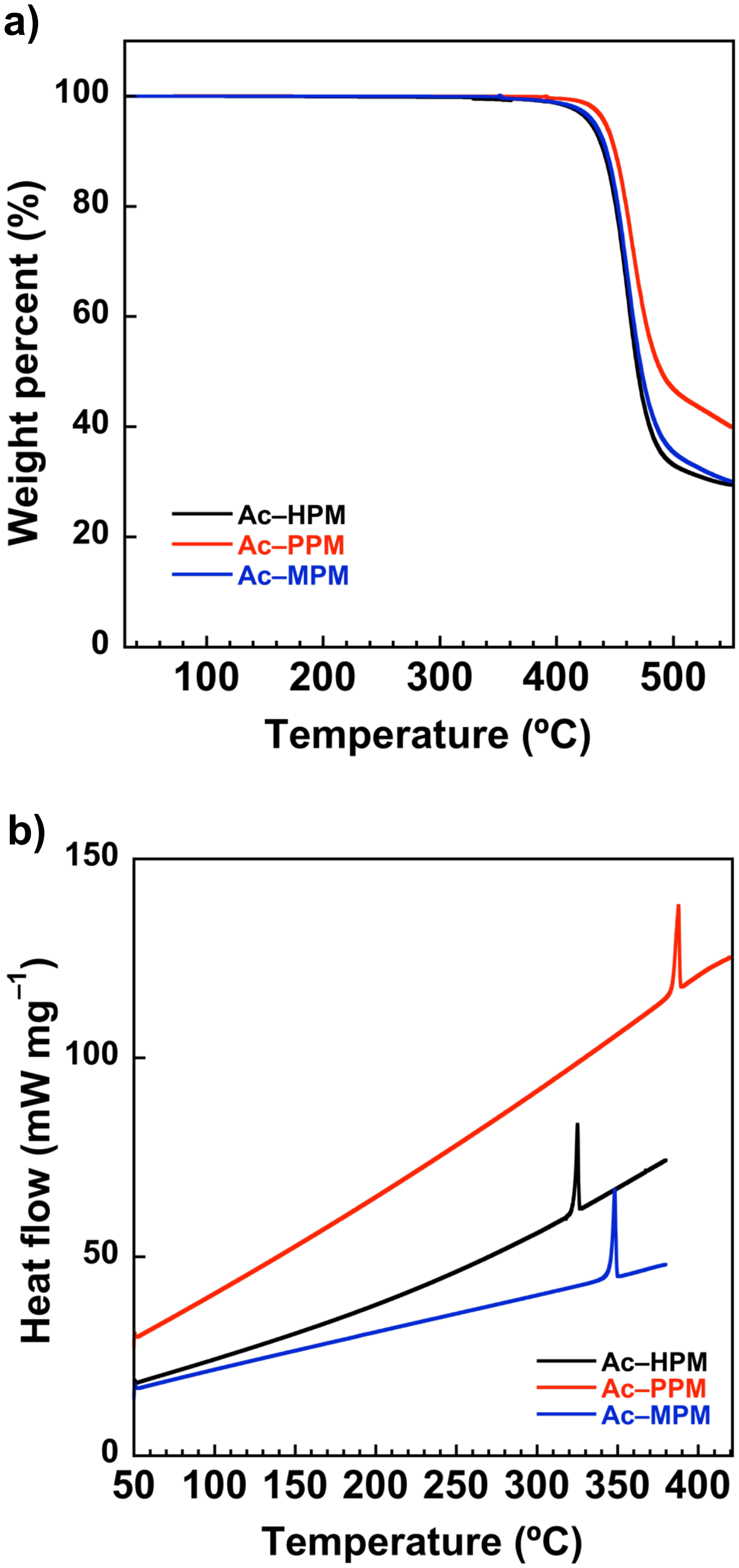


Figure S-2. a) TGA thermograms and b) DSC curves of **Ac–RPM** derivatives.

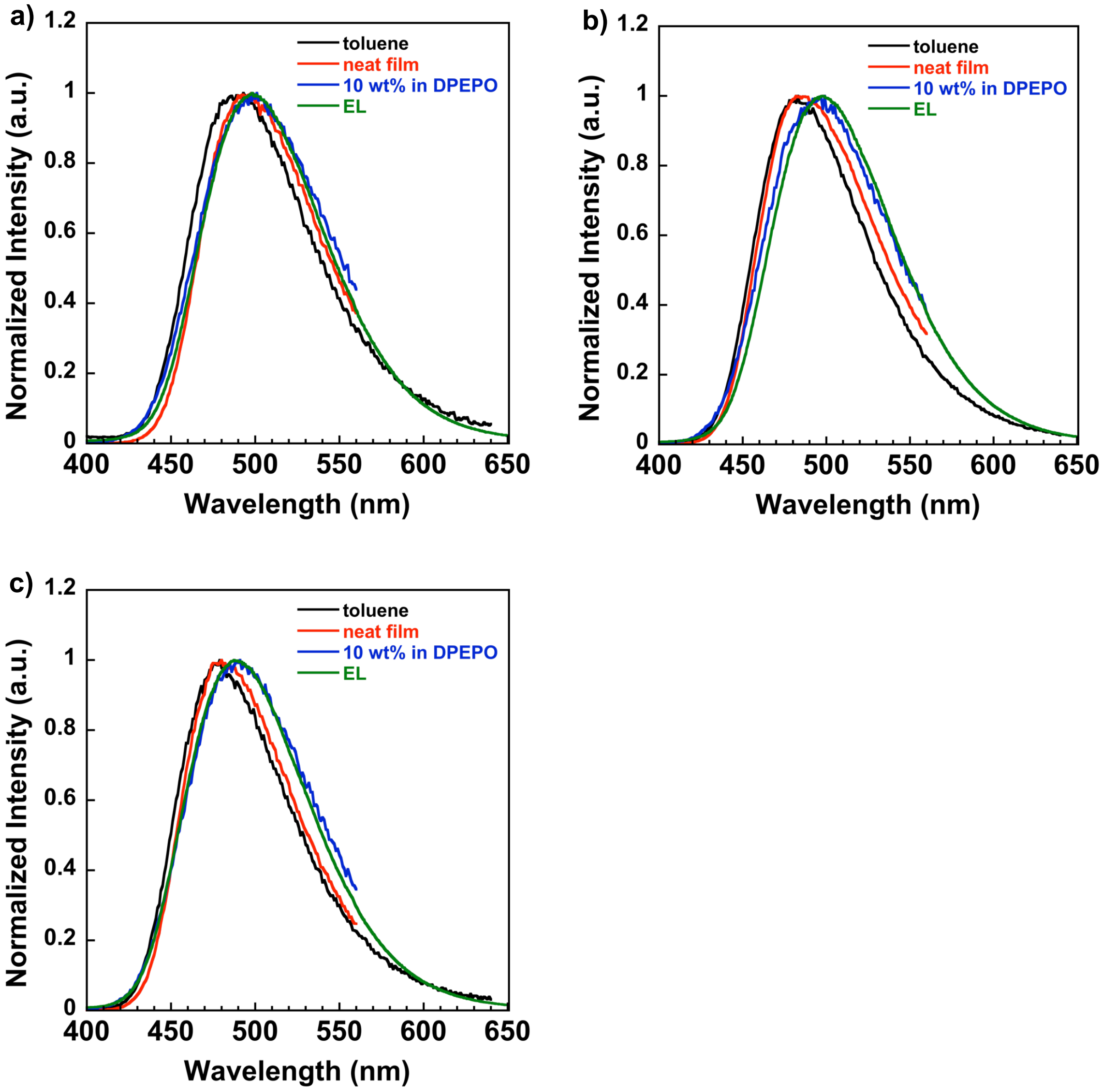


Figure S-3. PL spectra of toluene solution, neat film (30 nm), 10 wt% doped in DPEPO film (30 nm), and EL spectra of a) **Ac–HPM**, b) **Ac–PPM**, and c) **Ac–MPM**.

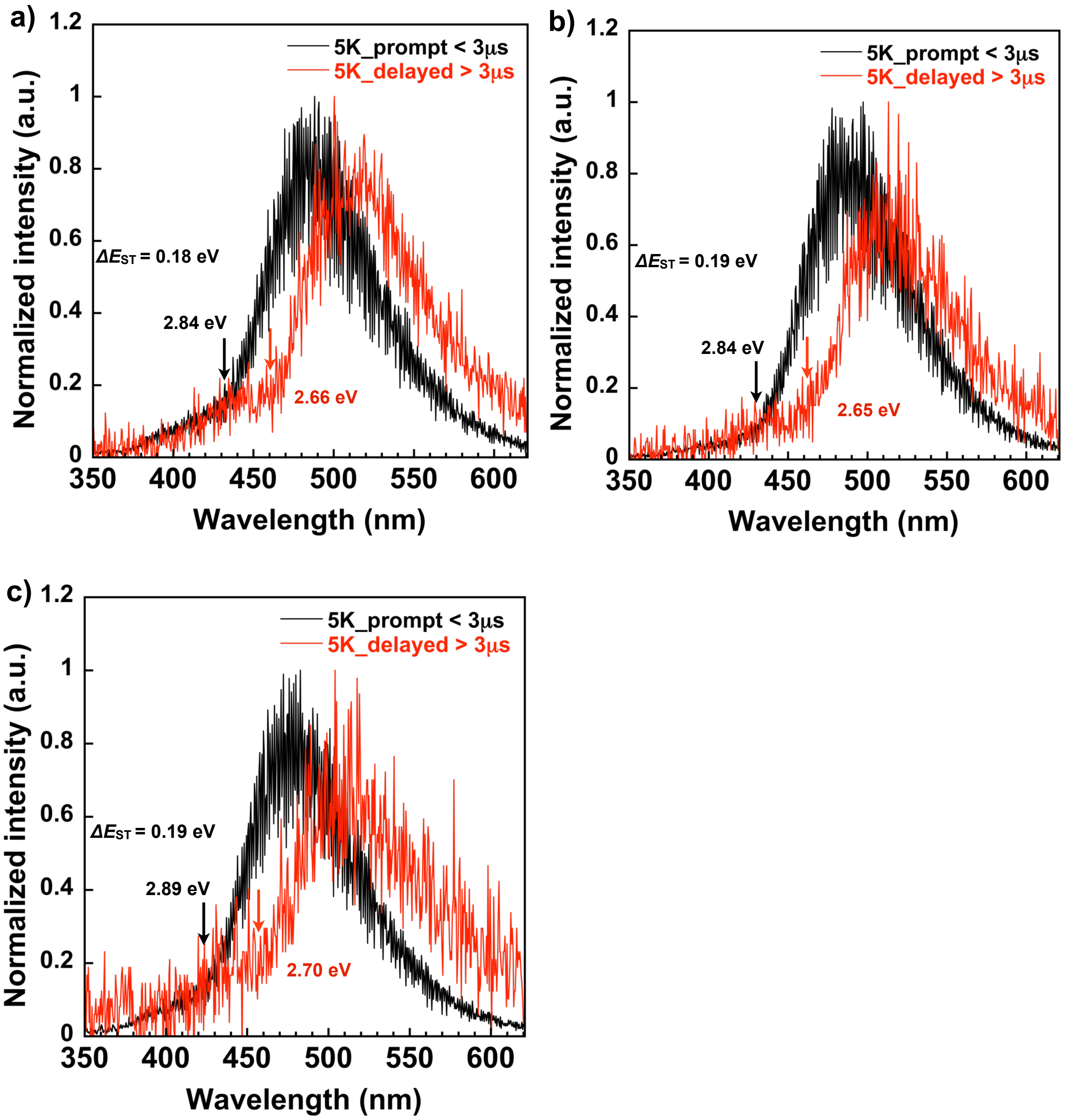
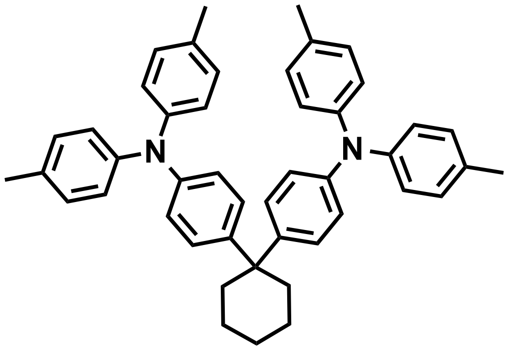
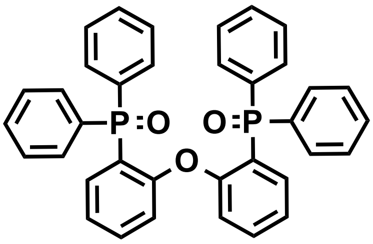


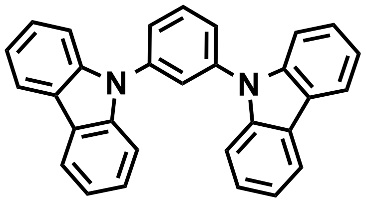
Figure S-4. Time resolved photoluminescence spectra of the a) **Ac–HPM-**, b) **Ac–PPM-**, and c) **Ac–MPM-**doped DPEPO film.



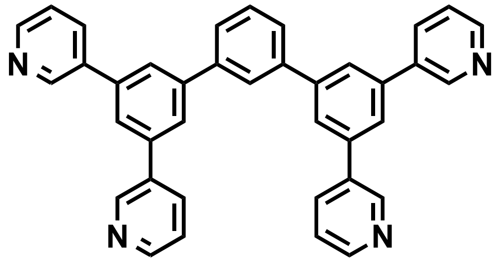
TAPC



DPEPO



mCP



B3PyPB

Figure S-5. Chemical structures of materials used in this work.

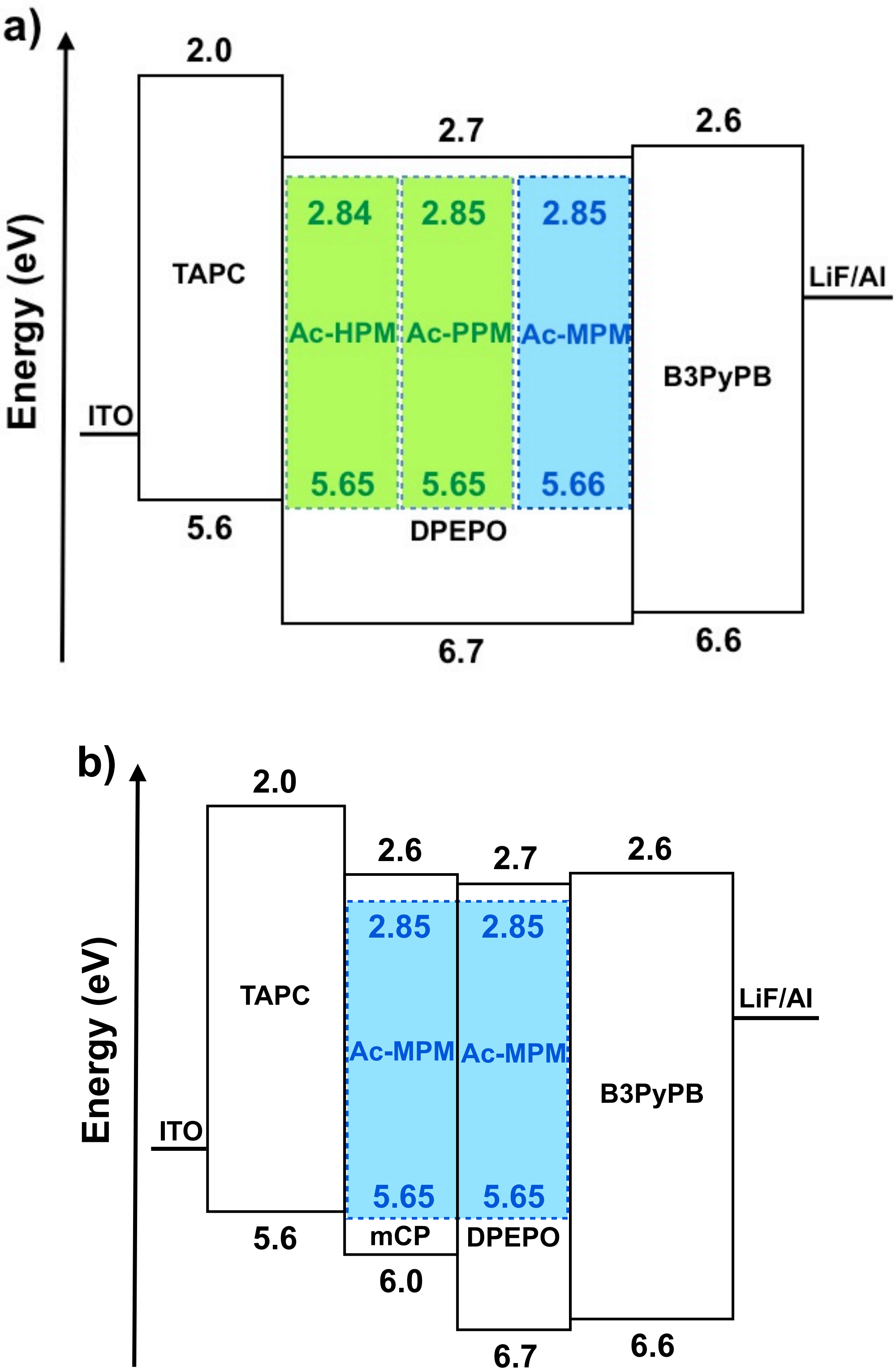


Figure S-6. Energy diagrams of **Ac–RPM**-based OLEDs.

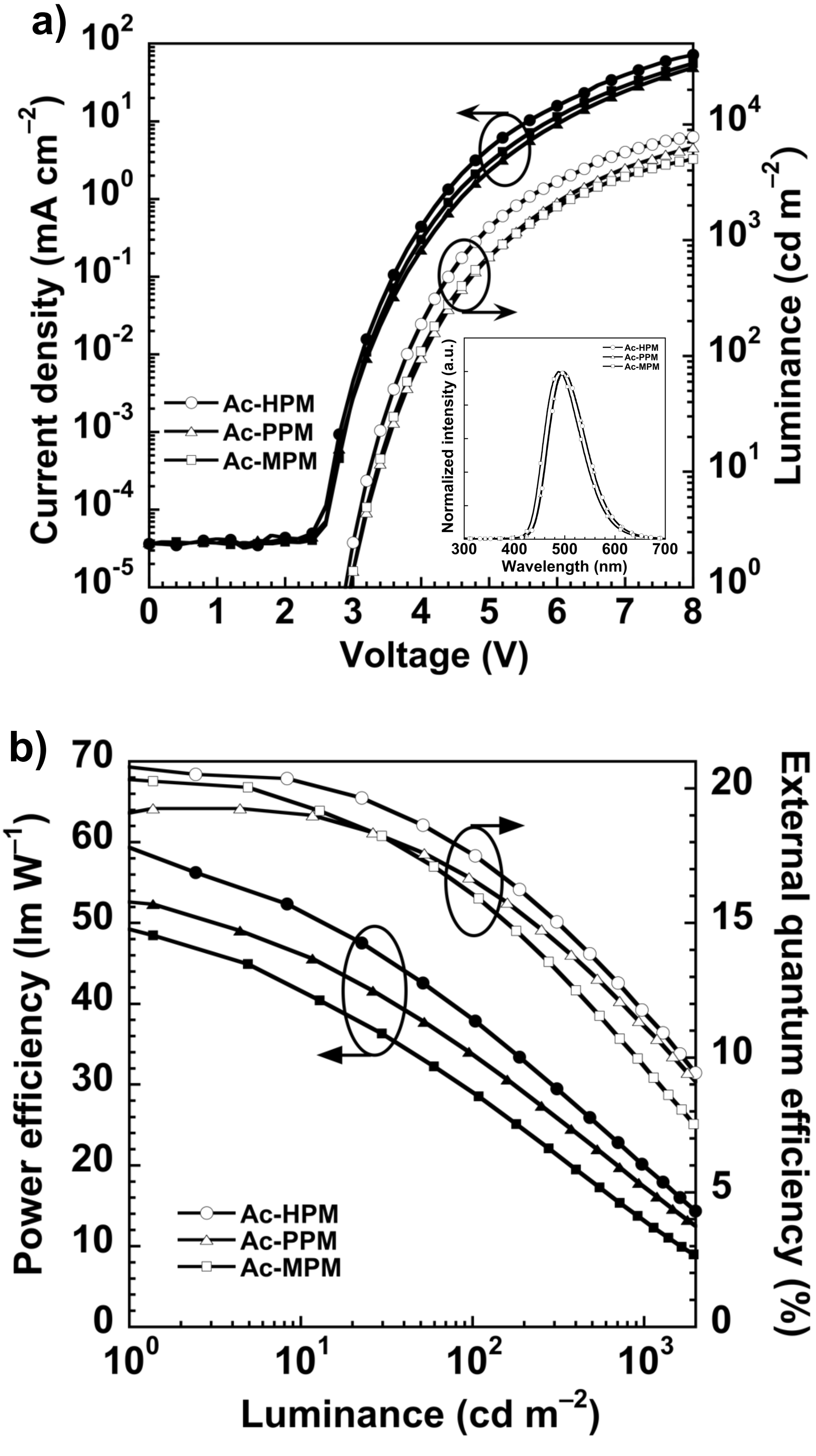


Figure S-7. a) *J–V–L* characteristics, inset: EL spectra at 0.5 mA, and b) *PE–EQE–L* characteristics of **Ac–RPM**-based OLEDs.

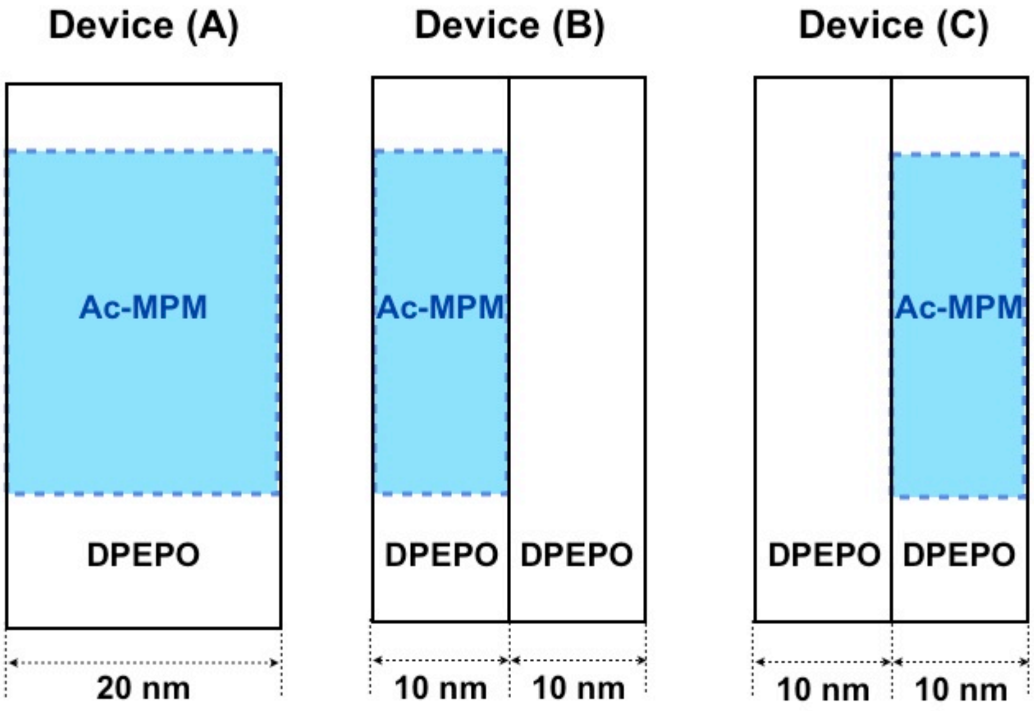


Figure S-8. Configuration of emissive layer in device (A)~(C).

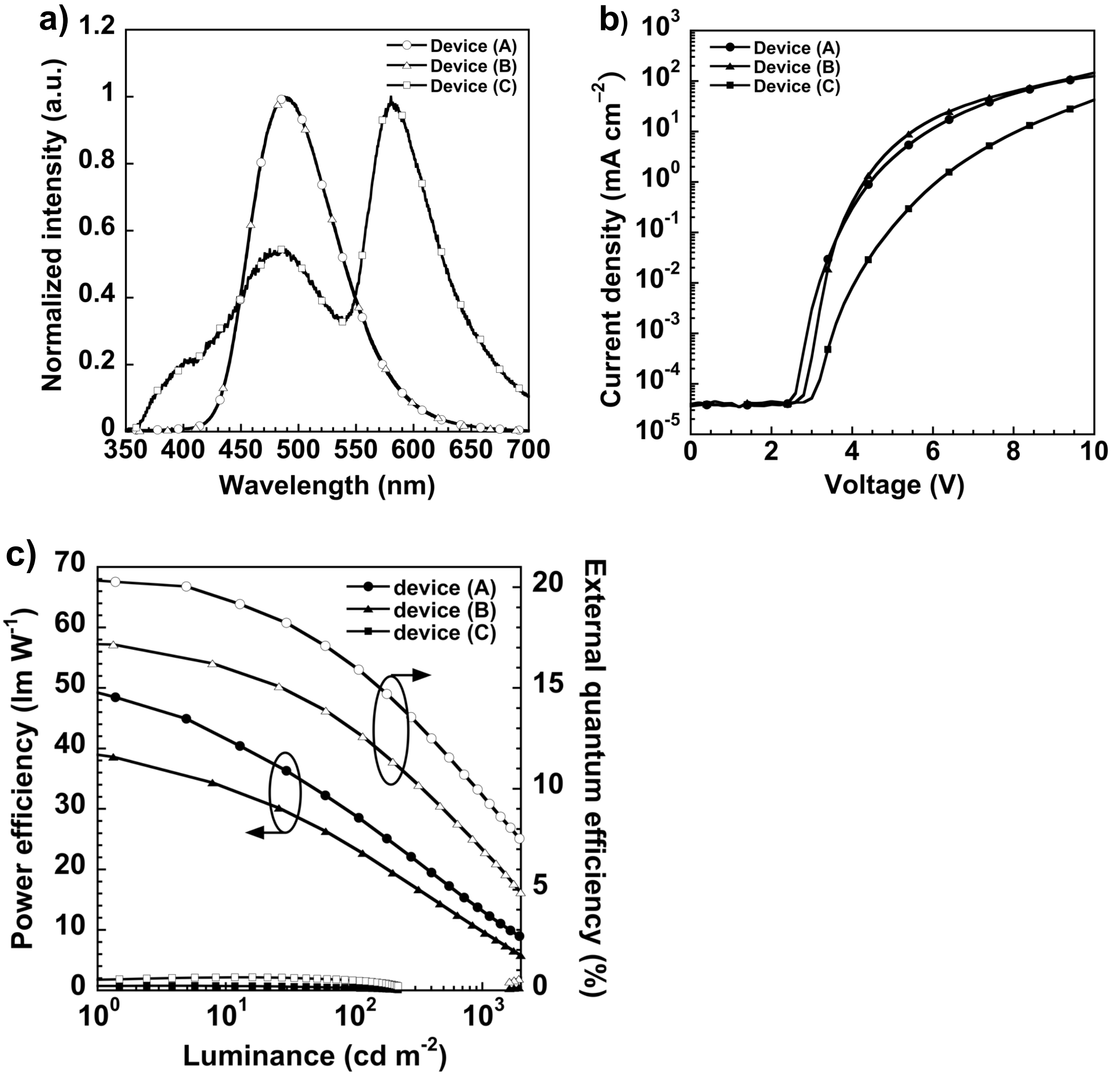


Figure S-9. a) EL spectra, b) *J–V*, and c) *PE–EQE–L* characteristics of device (A)~(C).

Table S-1. Calculated HOMO, LUMO, $\Delta E_{\mathrm{H\text{–}L}}$, E_{S}, E_{T} and ΔE_{ST} values (eV).

Compound	HOMO[a]	LUMO[a]	$\Delta E_{\mathrm{H\text{–}L}}$[b]	E_{S}[c]	E_{T}[c]	ΔE_{ST}[d]
Ac–HPM	–5.50	–2.19	3.31	2.85	2.84	0.01
Ac–PPM	–5.48	–2.11	3.37	2.90	2.89	0.01
Ac–MPM	–5.47	–2.09	3.38	2.91	2.90	0.01

[a] Calculated at RB3LYP 6-311+G(d,p)//RB3LYP 6-31G(d)· [b] $\Delta E_{\mathrm{H\text{–}L}}$ = HOMO–LUMO. [c] Lowest singlet (E_{S}) and triplet (E_{T}) energy from TD-DFT at RB3LYP 6-31G(d)//RB3LYP 6-31G(d). [d] Energy difference between E_{S} and E_{T} energy ($\Delta E_{\mathrm{ST}} = E_{\mathrm{S}} - E_{\mathrm{T}}$).

Table S-2. Summary of optical properties.

Compound	solution λ_{abs} [nm][a]	solution λ_{em} [nm][a]	film λ_{em} [nm][b]	doped film λ_{em} [nm][c]	EL λ_{em} [nm][d]	EL FWHM [nm][e]
Ac–HPM	378	489	496	498	499	86
Ac–PPM	381	484	486	498	498	86
Ac–MPM	375	478	482	489	489	87

[a] The absorption and emission peak of **Ac–RPM** in toluene (1.0×10^{-5} M). [b] The emission peak of **Ac–RPM** neat film. [c] The emission peak of 10 wt% **Ac–RPM**-doped DPEPO film. [d] The emission peak of **Ac–RPM**-based device. [e] The full width a half maximum (FWHM) of **Ac–RPM**-based device.

Table S-3. Summary of OLED performances.

Device	V_{on}/ $\eta_{\mathrm{p,\,on}}$/$\eta_{\mathrm{c,\,on}}$/ EQE [V/ lm W^{-1}/ cd A^{-1}/ %][a]	V_{100}/ $\eta_{\mathrm{p,\,100}}$/$\eta_{\mathrm{c,\,100}}$/ EQE [V/ lm W^{-1}/ cd A^{-1}/ %][b]	V_{1000}/$\eta_{\mathrm{p,\,1000}}$/$\eta_{\mathrm{c,\,1000}}$/ EQE [V/ lm W^{-1}/ cd A^{-1}/ %][c]	CIE (x, y)[d]
(A)	2.93 / 49.9 / 46.6 / 20.4	3.96 / 29.2 / 36.8 / 16.1	5.27 / 13.2 / 22.1 / 9.7	(0.19, 0.37)
(B)	3.14 / 39.4 / 39.4 / 17.2	3.94 / 23.8 / 29.7 / 13.0	5.15 / 9.79 / 16.0 / 7.0	(0.19, 0.37)
(C)	4.84 / 0.7 / 1.1 / 0.5	8.03 / 0.4 / 1.0 / 0.5	– / – / – / –	(0.33, 0.34)

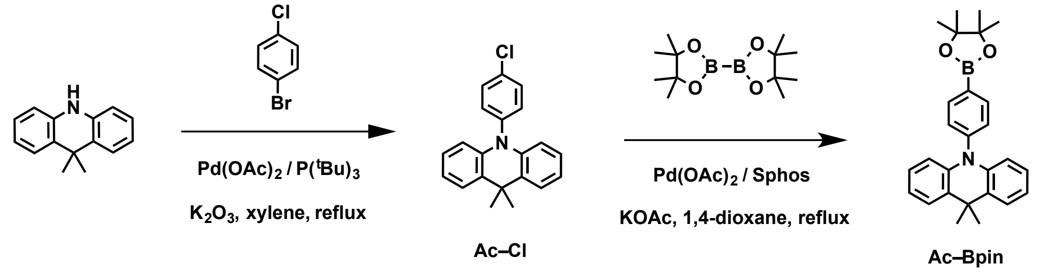
[a] Voltge (V), power efficiency (η_{p}), current efficiency (η_{c}) and external quantum efficiency (EQE) at 1 cd m^{-2}. [b] V, η_{p}, η_{c}, and EQE at 100 cd m^{-2}. [c] V, η_{p}, η_{c}, and EQE at 1000 cd m^{-2}. [d] CIE at 100 cd m^{-2}.

Table S-4. Summary of performances in blue TADF-OLED.

	V_{on} [a] [V]	$\eta_{p,100}/\eta_{\mathrm{ext},100}$ [b] [lm W^{-1}/%]	$\eta_{p,500}/\eta_{\mathrm{ext},500}$ [c] [lm W^{-1}/%]	$\eta_{p,1000}/\eta_{\mathrm{ext},1000}$ [d] [lm W^{-1}/%]	$\eta_{p,\mathrm{max}}/\eta_{\mathrm{ext,max}}$ [e] [lm W^{-1}/%]	CIE (x, y)
This work	2.8	34.0/17.2	20.6/12.3	15.5/10.1	61.6/24.5	(0.19,0.37)
Ref.[18]	3.7	-	-	-/16.0	-/19.5	(0.16,0.20)
Ref.[19]	(4.0)	-/17.1	-	-/10.4	-/20.6	(0.19,0.35)
Ref.[20]	(3.5)	-	-	-	-/20.1	(0.14,0.16)
Ref.[21]	3.20	-	-/11.3	-	-/21.2	(0.20,0.35)
Ref.[22]	(4.0)	-	18.0/16.7	-	42.7/25.0	(0.18,0.33)
Ref.[23]	3.00	-	-	9.8/10.6	30.4/22.3	(0.15,0.20)

[a] Voltage (V) at 1 cd m^{-2}. [b] Power efficiency (η_{p}) and external quantum efficiency (η_{ext}) at 100 cd m^{-2}. [c] η_{p}, η_{ext} at 500 cd m^{-2} [d] η_{p}, η_{ext} at 1000 cd m^{-2}. [e] Maximum power efficiency ($\eta_{\mathrm{p,max}}$), maximum external quantum efficiency ($\eta_{\mathrm{ext,max}}$).

Synthetic procedure



Synthesis of Ac–Cl:

9,9-Dimethyl-9,10-dihydroacridine (3.5 g, 16.7 mmol), 1-bromo-chlorobenzene (3.19 g, 16.7 mmol), and K_2CO_3 (6.9 g, 50 mmol) were added to a round bottom flask. Xylene (200 ml) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd(OAc)_2$ (0.19 g, 0.84 mmol) and $P(tBu)_3$ (0.6 ml, 2.5 mmol) were added and the resultant mixture was stirred for 48 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 10:1) to afford **Ac–Cl** (3.2 g, 60%) as a yellow solid: ^{1}H-NMR (400MHz,DMSO-d_6) : δ = 7.75 (d, 2H, *J*=8.8 Hz), 7.49 (dd, 2H, *J*=7.6, 1.2 Hz), 7.41 (d, 2H, *J*=8.4 Hz), 7.01–6.89 (m, 4H), 6.14 (dd, 2H, *J*=8.4, 1.2 Hz), 1.61 (s, 6H) ppm.

Synthesis of Ac–Bpin:

Ac–Cl (3.2 g, 10.0 mmol), KOAc (2.9 g, 30 mmol), 4,4,4',4',5,5,5',5',-octamethyl-2-2'-bi-1,3,2-dioxaborolane (3.05 g, 12 mmol) were added to a round bottom flask. 1,4-Dioxane (100 ml) was added, and nitrogen bubbled through the mixture for 1 hour. Then, $Pd(OAc)_2$ (110 mg, 0.5 mmol) and SPhos (0.2 g, 0.5 mmol) were added and the resultant mixture was stirred for 2 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 10:1) to afford **Ac–Bpin** (2.45 g, 60%) as a pale yellow solid: ^{1}H-NMR (400MHz,DMSO) : δ = 7.98 (d, 2H, *J*=8.4 Hz), 7.48 (dd, 2H, *J*=8.0, 2.0 Hz), 7.37 (d, 2H, *J*=8.4 Hz), 6.98–6.88 (m, 4H), 6.13 (dd, 2H, *J*=8.0, 1.2 Hz), 1.61 (s, 6H), 1.34 (s, 12H) ppm.

Synthesis of Ac–HPM:

Ac–Bpin (1.50 g, 3.65 mmol) and 4,6-dichloropyrimidine (0.27g, 1.73 mmol) were added to a round bottom flask. 1,4-dioxane (30 ml) and aqueous K_3PO_4 (1.35 M, 6.8 ml) were added and nitrogen was was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (170 mg, 0.18 mmol) and Sphos (75 mg, 0.18 mmol) were added and the resultant mixture was stirred for 4 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/ethyl acetate =

10:1 v/v) to afford **Ac–HPM** (0.45 g, 38%) as a yellow solid: ^{1}H-NMR (400 MHz,CDCl$_3$) : δ = 9.43 (d, 1H, *J*=1.2 Hz), 8.45 (d, 4H, *J*=8.8 Hz), 8.30 (d, 1H, *J*=1.6 Hz), 7.55 (d, 4H, *J*=8.4 Hz), 7.48 (dd, 4H, *J*=7.6, 1.6 Hz), 7.01–6.93 (m, 8H), 6.35 (dd, 4H, *J*=8.0, 1.6 Hz), 1.71 (s, 12H) ppm ; ^{13}C-NMR (100 MHz, CDCl$_3$) : δ = 164.19, 159.45, 144.05, 140.57, 136.75, 132.06, 130.20, 129.85, 126.42, 125.38, 120.8, 114.06, 113.14, 36.01, 31.29 ppm; MS: m/z = 648 [M+H]$^+$; Anal calcd for $C_{46}H_{38}N_4$: C, 85.42; H, 5.92; N, 8.66%. Found: C, 85.55; H, 5.90; N, 8.67%.

Synthesis of Ac–PPM:

Ac–Bpin (1.42 g, 3.45 mmol) and 4,6-dichloro-2-phenylpyrimidine (0.39g, 1.73 mmol) were added to a round bottom flask. 1,4-dioxane (30 ml) and aqueous K_3PO_4 (1.35 M, 6.4 ml) were added and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (160 mg, 0.17 mmol) and Sphos (70 mg, 0.17 mmol) were added and the resultant mixture was stirred for 2 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: chloroform) to afford **Ac–PPM** (0.82 g, 67%) as a yellow solid: ^{1}H-NMR (400 MHz,CDCl$_3$) : δ = 8.80 (dd, 2H, *J*=8.0, 1.6 Hz), 8.59 (d, 4H, *J*=8.8 Hz), 8.20 (s, 1H), 7.59–7.48 (m, 11H), 7.59–6.94 (m, 8H), 6.38 (dd, 4H, *J*=8.0, 1.2 Hz), 1.72 (s, 12H) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$) : δ = 164.87, 164.26, 143.86, 140.64, 137.79, 137.26, 131.96, 130.99, 130.15, 129.94, 128.61, 128.53, 126.44, 125.38, 120.81, 114.09, 110.65, 36.02, 31.33 ppm ; MS: m/z = 724 [M+H]$^+$; Anal calcd for $C_{52}H_{42}N_4$: C, 86.39; H, 5.86; N, 7.75%. Found: C, 86.19; H, 5.81; N, 7.78%.

Synthesis of Ac–MPM:

Ac–Bpin (1.50 g, 3.65 mmol) and 4,6-dichloro-2-methylpyrimidine (0.30g, 1.73 mmol) were added to a round bottom flask. 1,4-dioxane (30 ml) and aqueous K_3PO_4 (1.35 M, 6.8 ml) were added and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (170 mg, 0.18 mmol) and Sphos (75 mg, 0.18 mmol) were added and the resultant mixture was stirred for 4 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: chloroform) to afford **Ac–MPM** (0.28 g, 23%) as a pale yellow solid: ^{1}H-NMR (400 MHz, CDCl$_3$) : δ = 8.42 (d, 4H, *J*=8.8 Hz), 8.08 (s,1H), 7.54–7.47 (m, 8H), 7.00–6.90 (m, 8H), 6.34 (dd, 4H, *J*=8.0, 1.6 Hz), 2.95 (s, 3H), 1.71 (s, 12H) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$) : δ = 169.02, 164.41, 143.74, 140.61, 137.29, 132.04, 130.12, 129.94, 126.40, 125.39, 120.79, 114.06, 110.51, 36.01, 31.35, 26.58 ppm; MS: m/z = 661 [M+H]$^+$; Anal calcd for $C_{47}H_{40}N_4$: C, 85.42; H, 6.10; N, 8.48%. Found: C, 85.47; H, 6.06; N, 8.49%.