

# Molecular design of thermally activated delayed fluorescent emitters using 2,2'-bipyrimidine as an acceptor in donor-acceptor structure

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# Abstract

D-A-D type thermally activated delayed fluorescence (TADF) emitters, 5,5'-bis(4-(9,9 dimethylacridin-10(9H)-yl)phenyl)-2,2'-bipyrimidine (Ac-bpm) and 5,5'-bis(4-(10H-phenoxazin 10-yl)phenyl)-2,2'-bipyrimidine (Px-bpm), based on 2,2'-bipyrimidine accepting unit were developed and their TADF devices were fabricated. The orthogonal geometry between the dono unit and the 2,2'-bipyrimidine accepting core facilitated a HOMO/LUMO spatial separation, thus realizing thermally activated delayed fluorescence. They exhibited electroluminescence ranging from green to yellow, depending on the donor unit, with a maximum external quantum efficiencies of up to 17.1%.

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# Introduction

Recently, thermally activated delayed fluorescent (TADF) materials have emerged as an emissive dopant in organic light-emitting diodes (OLEDs) due primarily to their high external quantum efficiencies comparable to that of conventional phosphorescent emitter.<sup>1-2</sup> The high efficiencies are practicable by harvesting both singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) excitons through efficient reverse intersystem crossing (RISC) in which the T<sub>1</sub> can be up-converted to the S<sub>1</sub> by thermal activation.<sup>3</sup>

The efficient RISC can be generated by a small energy splitting ( $\Delta E_{ST}$ ) between the S<sub>1</sub> and T states of the TADF materials, so that twisted structures composed of electron donor (D) and acceptor (A) units are required for the highest occupied molecular orbital (HOMO)/lowes unoccupied molecular orbital (LUMO) separation which causes a small  $\Delta E_{ST}$ . Therefore, TADI materials are based on the design such as D-A or D-A-D molecular framework having a strong electron-donating and -accepting ability. However, unlike D units, the range of choice for usable A units is limited. Electron-deficient aromatic systems such as triazine,<sup>9-11</sup> triazole<sup>4</sup> and oxadiazole<sup>12</sup> are generally considered as A units. Furthermore, fragments such as sulfone,<sup>13,1</sup> phenone<sup>15,16</sup>, phenylborane<sup>17</sup> have been reported as alternative acceptors for TADF emitter. More recently, pyrimidine-based acceptor units have been developed as a new building block for TADI materials.<sup>18,19</sup> These TADF materials are appropriate as sky-blue or blue emitters because of les electron-deficient character compared with 1,3,5-triazine and the consequent increase of the band gap energy, so that tuning the energy gap through the modification of pyrimidine unit is required.

Herein, we report twisted D-A-D type TADF molecules comprising a 2,2'-bipyrimidine accepting core coupled with acridine or phenoxazine donor unit through a phenyl linker. Owing to the coplanar structure between each pyrimidine unit, a 2,2'-bipyrimidine core has more electrondeficient nature compared with a single pyrimidine unit, giving deeper LUMO levels and decreased energy band gaps. The new emitters reported in this work demonstrated the green electroluminescence (EL) emission and the rather high efficiency.

#### **Results and discussion**

#### Synthesis and theoretical calculations

The two new materials, Ac-bpm and Px-bpm were prepared using the procedures shown in Scheme 1. For access to two materials, firstly, the dibrominated bipyrimidine acceptor, 5,5' dibromo-2,2'-bipyrimidine (2Br-bpm), was prepared by bromination of 2,2'-bipyrimidine<sup>20</sup> with molecular bromine. Secondly, (4-(9,9-dimethylacridin-10(9H)-yl)phenyl)boronic acid (A2) and (4-(10H-phenoxazin-10-yl)phenyl)boronic acid (B2) were prepared in two steps starting from 9,9 dimethyl-9,10-dihydroacridine and phenoxazine, respectively. The two donor units, A2 and B2 were coupled with 2Br-bpm by Suzuki reaction, giving 5,5'-bis(4-(9,9-dimethylacridin-10(9H) and 5,5'-bis(4-(10H-phenoxazin-10-yl)phenyl)-2,2' yl)phenyl)-2,2'-bipyrimidine (Ac-bpm) bipyrimidine (Px-bpm) in moderate yields. As shown in Fig. 1, the geometry optimization and the electron densities of Ac-bpm and Px-bpm were performed via TD-DFT using the B3LYP/6-31G<sup>3</sup> basis set of Gaussian 09 program. For Ac-bpm and Px-bpm, the donor units were perpendicular to the phenyl linker (dihedral angle ~ 90°), whereas the dihedral angles between the central 2,2' bipyrimidine and the phenyl linker are 36.6° and 37.4°, respectively, resulting in HOMO/LUMO spatial separation which is critical factor for a small singlet-triplet splitting energy For a central core of Ac-bpm, a twist angle between each pyrimidine unit was calculated to be 17.3°, while Px-bpm displayed a coplanar central core. As depicted in Fig. 2a, the structure of Px bpm was further confirmed by X-ray diffraction analysis. Single crystals of Px-bpm were grown by a low pressure sublimation at 300 °C. The phenyl linker is nearly perpendicular to the phenoxazine donor (dihedral angle ~  $79^{\circ}$ ), whereas the twist angle between the phenyl linker and the 2,2'-bipyrimidine core was determined to be 40.8°. In addition, the central 2,2'-bipyrimidine core showed a coplanar geometry. As shown in Fig. 2b, Px-bpm displayed a zig-zag type arrangement in an intermolecular stacking. The orthogonal arrangement between the donor and the acceptor units is expected to reduce the intermolecular interactions, thus preventing the excimer emission.

#### Physical and electrochemical properties

The UV-vis absorption of emitters in tetrahydrofuran solution, photoluminescence (PL) and phosphorescence spectra in the doped solid film in the host material are shown in Fig. 3, and the data are summarized in Table 1. For Ac-bpm, the intense band at around 300 nm is attributable to the  $\pi$ - $\pi$ \* transitions, and weak band ranging from 350 to 450 nm is ascribed to the n- $\pi$ \* transition Compared to Ac-bpm, the absorption bands of Px-bpm are slightly bathochromic-shifted presumably due to the stronger donating ability of phenoxazine. Singlet and triplet energies o Ac-bpm were calculated to be 2.98 and 2.70 eV, respectively, whereas those of Px-bpm were estimated to be 2.79 and 2.63 eV in polystyrene film. The singlet-triplet splitting energy gap were 0.28 and 0.16 eV for Ac-bpm and Px-bpm, respectively. For Ac-bpm and Px-bpm doped into host materials, photoluminescence quantum yields (PLQYs) were 54% and 28% unde atmosphere, and 75% and 38% in oxygen-free condition from integrating sphere measurement respectively. The quantum yields diminished with an increase in doping concentration possibly because of the aggregation-induced quenching effect of the stick-like structure (Fig. S7).

The ionization potentials (IPs) and electron affinities (EAs) of Ac-bpm and Px-bpm were calculated from the onset potentials of redox curves using cyclic voltammetry measurement (CV (Fig. S1). Due to the electron-rich effect of phenoxazine unit relative to acridine unit, Px-bpm ha a less negative IP (-5.70 eV) compared to that (-5.84 eV) of Ac-bpm. EAs of Ac-bpm and Px-bpm are nearly the same (-3.13 and -3.15 eV, respectively) because EAs stem from the reduction of the same acceptor unit, 2,2'-bipyrimidine.

To prove the TADF character of Ac-bpm and Px-bpm, transient PL measurement was conducted with films of bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO): Ac-bpm (20 wt%) and 1,3-bis(*N*-carbazolyl)benzene (mCP): 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi): Px-bpm (3 wt%) at room temperature (Fig. 4). The two emitters display both prompt and delayed components, indicating the TADF behaviour. The excited state lifetimes of the delayed components were reported to be 37.5 and 25.0  $\mu$ s for Ac-bpm and Px-bpm, respectively. Furthermore, the delayed component increased with rising of temperature from 10( K to 297 K, proving the characteristic of TADF behaviour (Fig. S2).

As shown in Fig. S3, thermal properties of Ac-bpm and Px-bpm were studied using therma gravimetric analysis (TGA). Ac-bpm and Px-bpm showed good thermal stability with decomposition temperature ( $T_d$ , corresponding to 5% weight loss) of 442 °C and 504 °C respectively. In contrast, glass transitions were not observed in both emitters.

#### **Electroluminescence properties**

The EL performances of Ac-bpm and Px-bpm were evaluated in TADF devices fabricated with the following two configurations: [Single-host system, Device A] ITO/PEDOT:PSS (6( nm)/TAPC (20 nm)/mCP (10 nm)/DPEPO:Ac-bpm or Px-bpm (25 nm, x%)/TSPO1 (5 nm)/TPB (20 nm)/LiF (1.5 nm)/Al (200 nm), x = 10-30% and [Mixed-host system, Device B ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/mCP:TPBi:Ac-bpm or Px-bpm (25 nm x%)/TSPO1 (5 nm)/TPBi (40 nm)/LiF (1.5 nm)/Al (200 nm), x = 3-10% (Fig. 5). *N,N* Dicarbazolyl-3,5-benzene (mCP) and diphenyl-4-triphenylsilylphenyl phosphine oxide (TSPO1 between the emission layer and charge transporting layer were employed as the hole- and electron-transport type exciton blocking layer, respectively. The device characteristics are shown in Fig. 6 and Fig. S5, S6, and device performances are summarized in Table 2. In the device A, the direct charge trapping on an emitter could be the main EL mechanism, presumably due to the deeper LUMO and shallower HOMO energy levels relative to those of DPEPO host material. In the device B, in contrast, the host-dopant energy transfer would be a predominant EL mechanism because HOMO and LUMO energy levels of mixed host materials are comparable to those of adjacent transport layers. As shown in Fig. 6, Ac-bpm based device A and Px-bpm based device B displayed EL emissions with peaks of 517 and 547 nm, and CIE coordinates of (0.29, 0.53) and (0.41, 0.54), respectively.

Ac-bpm exhibited an EQE of 17.1 % in 20% doping concentration, whereas Px-bpm showed a reduced EQE (4.6%) in the same doping concentration. To study the origin of the low EQE of the Px-bpm device, single carrier devices were prepared. As shown in Fig. S6, the hole-only and electron-only devices were fabricated with the structures of PEDOT (60 nm)/TAPC (20 nm)/mCI (10 nm)/DPEPO:Ac-bpm or Px-bpm (25 nm, 20%)/TAPC (5 nm)/Al (200 nm) and PEDOT (60 nm)/TSPO1 (10 nm)/DPEPO:Ac-bpm or Px-bpm (25 nm, 20%)/TSPO1 (5 nm)/TPBi (40 nm)/LiI (1.5 nm)/Al (200 nm), respectively. There was little difference of the hole and electron density in the two devices, suggesting that carrier imbalance is not the reason for the low EQE of the Px bpm devices. Therefore, the low EQE of the Px-bpm device is due to strong intermolecula interaction induced quenching because of high doping concentration. At low doping concentration carrier imbalance reduced the EQE and intermolecular quenching decreased the EQE at high doping concentration. To improve the EQE, emitters were tested in mCP:TPBi mixed-host device B in which mCP and TPBi were used as a hole-transport-type and an electron-transport-type hos respectively, and the EQE of Px-bpm reached up to 14.4% in 3% doping concentration. Ac-bpn based device showed the severe efficiency roll-off, primarily attributable to the longer T1 excited state lifetime,<sup>21</sup> whereas Px-bpm based device displayed a suppressed efficiency roll-off relative to Ac-bpm device. Furthermore, the efficiency roll-off of mixed host devices was generally suppressed compared to single host one owing to the enhanced charge balance.<sup>22</sup>

# Conclusions

In conclusion, we developed two novel D-A-D type TADF emitters, Ac-bpm and Px-bpm, composed of 2,2'-bipyrimidine as a new acceptor unit and acridine or phenoxazine as a donor unit. The perpendicularity of donor unit with respect to the 2,2'-bipyrimidine accepting core facilitates a HOMO/LUMO spatial separation, thus realizing thermally activated delayed fluorescence. Ac-bpm exhibited a green emission and a maximum EQE of 17.1% in single-host device. In contrast, Px-bpm showed a yellow emission with a maximum EQE of 14.4% in mixed-host device. A novel 2,2'-bipyrimidine accepting core allows the emission colour tuning through the combination with variou donor units.

#### **Experimental**

**Materials**. All reactions were carried out under nitrogen atmosphere unless otherwise noted. Standard Schlenk techniques were employed to manipulate air sensitive solutions while workup procedures were done in air. All solvents utilized in this work were obtained from Fisher Scientific (HPLC grade) unles otherwise noted. Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone and were subsequently distilled under nitrogen prior to use. All deuterated solvents were purchased from Aldrich 2,2'-bipyrimidine was prepared according to literature procedure.<sup>20</sup> Chromatographic purification (Silic Gel 60, 230-400 mesh, Merck) of all compounds was performed on the bench top.

**X-ray crystallography**. Single crystals of Px-bpm suitable for the X-ray crystallography were grown by a low pressure sublimation at 300 °C. Diffraction data were collected on a Bruker SMART X-ray diffractometer at room temperature using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) The structure was solved by direct methods (SHELXS-97) and refined against all  $F^2$  data (SHELX 97).<sup>23,24</sup> All non-hydrogen atoms were refined anisotropic thermal parameters, and the hydrogen atoms were treated as idealized contributions.

Instruments. <sup>1</sup>H NMR spectra were recorded on an Avans 500 MHz spectrometer and <sup>13</sup>C NMR spectra were recorded on an Avans III HD 850 MHz spectrometer. Chemical shifts for <sup>1</sup>H NMR spectra are

relative to a residual proton in the deuterated solvents (CDCl<sub>3</sub>,  $\delta = 7.24$  ppm). All coupling constants are reported in hertz. HRMS data were obtained at Korea Basic Science Institute. Electronic absorption spectra were recorded on a JASCO spectrophotometer. Cyclic voltammetry were performed by purging the acetonitrile (spectroscopic grade) solution by dry nitrogen gas for 10 min. The supporting electrolyte was 0.1 M tetrabultylammonium perchlorate (TBAClO<sub>4</sub>). Glassy carbon and Ag/AgCl (0.01 M NaCl) were used as a working and a reference electrode, respectively. The scan rate was maintained at 100 mV/s.

#### 5,5'-dibromo-2,2'-bipyrimidine (2Br-bpm)

2,2'-Bipyrimidine (1.87 g, 11.8 mmol), bromine (1.2 mL, 23.6 mmol) and nitrobenzene (25 mL) were placed in a sealed tube, and the solution was stirred for 48 h at 135 °C. The product was extracted with chloroform and washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> three times. The crude product was purified by column chromatography on silica gel. Elution with methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:100) gave 2Br-bpm as brown solid. Yield: 1.68 g (5.31 mmol, 45%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.03 (s, 4 H), MS (FAB) m/z 31: [(M+H)<sup>+</sup>].

# 10-(4-bromophenyl)-9,9-dimethyl-9,10-dihydroacridine (A1)

9,9-Dimethyl-9,10-dihydroacridine (5.0 g, 24.0 mmol), 1-bromo-4-iodobenzene (6.8 g, 24.0 mmol) copper(I) iodide (46 mg, 0.24 mmol), sodium *tert*-butoxide (3.45 g, 36.0 mmol) and trans-1,2 cyclohexanediamine (0.29 mL, 2.4 mmol) were added to 1,4-dioxane (100 mL). The mixture was stirred at 100 °C for 12 h, then cooled to room temperature. The product was extracted with chloroform and washed with brine three times. The crude product was purified by column chromatography on silica gel Elution with Hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) gave **A1** as white solid. Yield: 4.35 g (12.0 mmol, 50%). <sup>1</sup>H NMF (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, *J* = 9.0 Hz, 2 H), 7.46 (dd, *J*<sub>1</sub> = 1.5 Hz, *J*<sub>2</sub> = 7.5 Hz, 2 H), 7.22 (d, *J* = 8.: Hz, 2 H), 6.99-6.92 (m, 4 H), 6.25 (dd, *J*<sub>1</sub> = 1.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2 H), 1.68 (s, 6 H) ; MS (FAB) m/z 364 [(M+H)<sup>+</sup>].

#### (4-(9,9-dimethylacridin-10(9H)-yl)phenyl)boronic acid (A2)

*n*-BuLi (2.1 mL, 3.29 mmol) was added dropwise to a solution of **A1** (1.0 g, 2.75 mmol) and THF (40 mL) at -78 °C. After the solution was stirred for 30 min, B(OMe)<sub>3</sub> (0.46 mL, 4.13 mmol) was added. The mixture was stirred at room temperature for 12 h. The product was extracted with chloroform and washed with brine three times. The crude product was purified by column chromatography on silica gel. Elution with methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:100) gave **A2** as white solid. Yield: 0.60 g (1.82 mmol, 66%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.56 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.49 (dd, *J*<sub>1</sub> = 1.5 Hz, *J*<sub>2</sub> = 7.5 Hz, 2 H), 7.01-6.92 (m, 4 H), 6.33 (dd, *J*<sub>1</sub> = 1.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2 H), 1.72 (s, 6 H) ; MS (FAB) m/z 33<sup>1</sup> [(M+H)<sup>+</sup>].

# 5,5'-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-2,2'-bipyrimidine (Ac-bpm)

A2 (0.63 g, 1.9 mmol), 2Br-bpm (0.25 g, 0.79 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (91 mg, 0.08 mmol) and potassiun carbonate (0.66 g, 4.74 mmol) were added to a THF/water (10 mL/2 mL) solution. After the solution wa heated at 70 °C for 12 h, the reaction mixture was cooled to room temperature. The product was extracted with chloroform and washed with brine three times. The crude product was purified by column chromatography on silica gel. Elution with methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:100) gave Ac-bpm as yellow solid Yield: 0.35 g (0.48 mmol, 61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.41 (s, 4 H), 7.99 (d, *J* = 6.5 Hz, 4 H) 7.58 (d, *J* = 8.0 Hz, 4 H), 7.50 (dd, *J<sub>I</sub>* = 1.5 Hz, *J<sub>2</sub>* = 7.5 Hz, 4 H), 7.05-6.96 (m, 8 H), 6.34 (dd, *J<sub>I</sub>* = 1.0 Hz, *J<sub>2</sub>* = 8.0 Hz, 4 H), 1.63 (s, 12 H); <sup>13</sup>C NMR (214 MHz, CDCl<sub>3</sub>):  $\delta$  160.83, 156.12, 142.76, 140.63 133.76, 132.67, 130.24, 129.73, 126.47, 125.44, 120.93, 114.99, 114.03, 36.04, 31.30; MS (FAB) m/. 725 [(M+H)<sup>+</sup>].

# 10-(4-bromophenyl)-10H-phenoxazine (B1)

A procedure similar to that used for A1 was followed but with phenoxazine (4.38 g, 24.0 mmol) instead of 9,9-Dimethyl-9,10-dihydroacridine. Yield: 3.64 g (10.8 mmol, 45%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): =7.72 (d, J = 8.5 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 6.70-6.65 (m, 4 H), 6.60 (t, J = 8.0 Hz, 2 H), 5.91 (d, J = 7.5 Hz, 2 H); MS (FAB) m/z 338 [(M+H)<sup>+</sup>].

# (4-(10H-phenoxazin-10-yl)phenyl)boronic acid (B2)

A procedure similar to that used for A2 was followed but with B1 (1.0 g, 2.96 mmol) instead of A1. Yield: 0.58 g (1.92 mmol, 65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.50 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 5.0 Hz, 2 H), 6.73-6.60 (m, 6 H), 5.98 (br, 2 H); MS (FAB) m/z 304 [(M+H)<sup>+</sup>].

#### 5,5'-bis(4-(10H-phenoxazin-10-yl)phenyl)-2,2'-bipyrimidine (Px-bpm)

A procedure similar to that used for **Ac-bpm** was followed. **B2** (0.46 g, 1.52 mmol), **2Br-bpm** (0.20 g, 0.63 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (73 mg, 0.06 mmol), potassium carbonate (0.52 g, 3.78 mmol) and THF/water (10 mL/2 mL). Yield: 0.27 g (0.40 mmol, 63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.35 (s, 4 H), 7.95 (d, *J* = 8.: Hz, 4 H), 7.59 (d, *J* = 8.5 Hz, 4 H), 6.74 (d, *J* = 7.5 Hz, 4 H), 6.69 (t, *J* = 7.5 Hz, 4 H), 6.64 (t, *J* = 8.0 Hz 4 H), 6.02 (d, *J* = 8.0 Hz, 4 H); <sup>13</sup>C NMR (214 MHz, CDCl<sub>3</sub>): δ 161.04, 156.09, 143.97, 133.99, 133.93 133.39, 132.23, 129.90, 123.35, 123.32, 121.73, 115.68, 113.23; MS (FAB) m/z 673 [(M+H)<sup>+</sup>].

#### **Device Fabrication**

Device structure of the TADF OLEDs was indium tin oxide (50 nm)/PEDOT:PSS (poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate)) (60 nm)/TAPC (4,4'-cyclohexylidenebis[*N*,*N*-bis(4 methylphenyl)benzenamine]) (20 nm)/mCP (1,3-Bis(*N*-carbazolyl)benzene) (10 nm)/DPEPO (bis[2 (diphenylphosphino)phenyl]ether oxide):TADF dopant (25 nm)/TSPO1 (diphenyl-4-triphenylsilylphenyl phosphineoxide) (5 nm)/TPBi (2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole)) (20 nm)/LiF (1.5 nm)/Al (200 nm). Ac-bpm or Px-bpm were doped in the DPEPO at doping concentration range from 10% to 30%.

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#### List of tables

**Table 1**. Physical properties and TD-DFT results.

 Table 2. Summarized device performances of TADF devices.

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<b>Table 1.</b> Physical properties and TD-DFT re
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	Experimental						Calculated	
Emitter	$\lambda_{abs}{}^a$	$\lambda_{\mathrm{em}}{}^{b}$	${oldsymbol{\varPhi}_{\mathrm{air}}}/{oldsymbol{\varPhi}_{\mathrm{N2}}}^{c}$	= [ma]/= [ua]	$S_1/T_1/\Delta E_{ST}^d$	IP/EA [eV] <sup>e</sup>	HOMO/LUMO <sup>f</sup>	$S_{\rm l}/T_{\rm l}/\Delta E_{\rm ST}{}^{\rm g}$
	[nm]	[nm]	[%]	$\tau_{\rm p}[{\rm ns}]/\tau_{\rm d}[{\rm \mu s}]$	[eV]		[eV]	[eV]
Ac-bpm	287	471	54/75	63/37.5	2.98/2.70/0.28	-5.84/-3.13	-4.98/-2.17	2.44/2.44/0.00
Px-bpm	293	524	28/38	77/25.0	2.79/2.63/0.16	-5.70/-3.15	-4.75/-2.28	2.11/2.10/0.01

<sup>*a*</sup> Measured in THF solution. <sup>*b*</sup> Measured in polystyrene film (1 wt%). <sup>*c*</sup> Obtained from integrating sphere. <sup>*d*</sup> Singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) energies were estimated from onset wavelengths of the emission spectra at room temperature and 77 K in polystyrene films, respectively.  $\Delta E_{ST} = E_S - E_T$ . <sup>*e*</sup> Estimated from onset potentials of cyclic voltammetry. <sup>*f*</sup> Calculated by TD-DFT at B3LYP/6-31G\*. <sup>*g*</sup> S<sub>1</sub> and T<sub>1</sub> were the energies of the first singlet and triplet state.

# Table 2. Summarized device performances of TADF devices.

Device	Emitter	Doping conc. [%]	QE <sup>a</sup> [%]	$CE^b$ [cd A <sup>-1</sup> ]	PE <sup>c</sup> [lm W <sup>-1</sup> ]
		10	16.2	47.6	42.7
	Ac-bpm	20	17.1	52.8	48.1
٨		30	12.9	40.5	42.4
A		10	6.0	17.7	14.1
	Px-bpm	20	4.6	12.7	10.5
		30	3.5	9.2	7.6
		3	10.9	29.4	26.4
	Ac-bpm	5	13.6	38.3	34.4
р		10	12.7	36.3	32.6
Б	Px-bpm	3	14.4	42.4	33.3
		5	12.7	36.8	29.6
		10	11.6	33.1	29.4

<sup>a</sup> Maximum external quantum efficiency at 1,000 cd/m2. <sup>b</sup> Maximum current efficiency. <sup>c</sup> Maximum power efficiency.

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