Electronic supplementary information

Zinc complexes exhibiting highly efficient thermally activated delayed fluorescence and their application to organic light emitting diodes

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\textsuperscript{f} JST, ERATO, Adachi Molecular Exciton Engineering Project, c/o OPERA, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

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SI-1. General Methods

**General**

All reactions were carried out under N\textsubscript{2} atmospheres. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded in CDCl\textsubscript{3} with an Avance 500 spectrometer (Bruker Biospin, Germany). MALDI-TOF mass spectra were obtained on an Autoflex III spectrometer (Bruker Daltonics, Germany) in reflection/positive mode with dithranol as matrix. Elemental analyses (C, H, N) were carried out with a MT-5 CHN analyzer (Yamaco, Japan). The solution samples (1.0 \times 10^{-5} M) for the photoluminescence studies were degassed with nitrogen for several minutes prior to use unless otherwise indicated. Thin film samples (~100 nm) for the luminescence and photoelectron spectroscopy studies were deposited on quartz glass substrates by vacuum evaporation (pressure < 4 \times 10^{-4} Pa; rate \approx 0.2 nm/s) for Zn-1, Zn-2, OMe-1. Spin-cast films of 6-wt%-doped mCP were spin-coated from chloroform solution at 1500 rpm for 30 sec. UV-VIS absorption spectra of the compounds in toluene were measured on a Lambda 950-PKA UV/VIS spectrophotometer (Perkin-Elmer). The photoluminescence spectra were recorded on a FluoroMax-4 (Horiba Jobin Yvon). The absolute PL quantum yield ($\phi_{PL}$) was obtained using an integrating sphere (C9920-02, Hamamatsu Photonics Co.) with a multichannel spectrometer (PMA-11, Hamamatsu Co.). The transient photoluminescence decay characteristics of the film samples were investigated under vacuum conditions using a streak camera (C4334, Hamamatsu Photonics Co.) equipped with a N\textsubscript{2} gas laser (MNLL200, Laser Technik Berlin, $\lambda$ = 337 nm, pulse width \approx 500 ps, repetition rate = 20 Hz) as the excitation source. The HOMO energy levels of the compounds in film state were determined by atmospheric ultraviolet photoelectron spectroscopy using a Riken Keiki AC-3.

**OLED fabrication and measurement**

The Al-2' OLEDs were fabricated by standard wet and dry processes. First, PEDOT-PSS was spin-coated on a ITO glass substrate at 3000 rpm for 60 sec to form a 40-nm-thick layer, and the film was baked at 200 °C for 10 minutes. Next, an emissive layer (30 nm thick) was formed at 3000 rpm for 60 sec. The electron transport layer, LiF, and Al were vapor deposited on top of the emissive layer. The Zn-1, Zn-2 and OMe-1 OLEDs were fabricated entirely by vapor deposition. The organic and metal layers were deposited by thermal evaporation in a vacuum chamber with a base pressure of < 4.0 \times 10^{-4} Pa. Current density-voltage ($J$-$V$) characteristics were measured using a semiconductor parameter analyzer (HP4155C; Agilent Co.) with an optical power meter (Model 1835-C; Newport)
SI-2. Synthetic Route

1a

The reagents 4-bromo-2-hydroxybenzaldehyde (1.00 g, 3.4 mmol) and 2-aminophenol (3.15 g, 28.8 mmol) were added to 120 mL of acetic acid. After stirring for 30 min at room temperature, lead(IV) acetate (11.7 g, 26.4 mmol) was added to the mixture. The reaction mixture was stirred for 1 hour and then gently boiled at 110 °C overnight. The mixture was cooled, poured into cold water, and neutralized with aqueous NaOH solution. The precipitate was filtered, extracted in ethyl acetate, and dried with MgSO₄. After the solvent was removed, the crude product was purified by using silica gel column chromatography with hexane/dichloromethane (7/3 by volume).

2-(benzo[d]oxazol-2-yl)-5-bromophenol (1a) was obtained as a yellow powder (3.25 g, yield: 46.7%).

1H NMR (500 MHz, CDCl₃): δ (ppm) 11.6 (1H), 7.88 (d, J=8.5 Hz, 1H), 7.75-7.73 (m, 1H), 7.63-7.60 (m, 1H), 7.41-7.39 (m, 2H), 7.33 (d, J=2.0 Hz, 1H), 7.16 (dd, J=2.0 Hz, J=1.5 Hz, 1H).

13C NMR (125 MHz, CDCl₃): δ (ppm); 159.19, 149.09, 128.01, 125.67, 125.22, 123.06, 120.76, 119.34, 109.67; Anal. Calcd. for C₁₃H₈BrNO₂: C, 53.82; H, 2.78; N, 4.83. Found C, 53.70; H, 2.72; N, 4.78.

2a

Compound 1a (1.00 g, 3.46 mmol) and cesium carbonate (1.18 g, 3.63 mmol) were dissolved in CH₃CN (17 mL). Benzyl bromide (0.42 ml, 3.53 mmol) was added and the mixture was heated to 80 °C for 2.5 hours. The reaction mixture was then allowed to cool to room temperature and filtered. The filtrate was diluted with dichloromethane. The organic layer was washed with 0.2 N NaOH aqueous solution and brine, dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure. It was recrystallized from hexane.

2-(2-(benzyloxy)-4-bromophenyl)benzo[d]oxazole (2a) was obtained as a yellow powder (1.01 g, yield: 76.5%).

1H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (d, J=8.0 Hz, 1H), 7.84-7.82 (m, 1H), 7.62-7.58 (m, 3H), 7.45-7.42 (m, 2H), 7.40-7.36 (m, 3H), 7.32-7.30 (m, 2H), 5.32 (s, 2H).

13C NMR (125 MHz, CDCl₃): δ (ppm); 161.21, 157.82, 150.66, 141.87, 136.08, 132.39, 128.57, 128.00, 126.89, 126.57, 125.12, 124.53, 124.47, 120.14, 117.54, 116.11, 110.50, 71.11; Anal. Calcd. for C₂₀H₁₄BrNO₂: C, 63.18; H, 3.71; N, 3.68. Found C, 63.11; H, 3.64; N, 3.66.
Compound 2a (1.14 g, 3.00 mmol), phenoxazine (0.69 g, 3.75 mmol), potassium carbonate (1.24 g, 9.0 mmol), and palladium(II) acetate (0.07 g, 0.3 mmol) were dissolved in toluene (15 ml). Tri-tert-butylphosphine (2M toluene solution 0.33 mmol) was added in the mixture and then was stirred and refluxed overnight. The cooled mixture was partitioned between dichloromethane and water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over MgSO$_4$, and concentrated in vacuo. The crude product was purified by using silica gel column chromatography with hexane/dichloromethane (1/1 by volume).

10-(4-(benzo[d]oxazol-2-yl)-3-(benzyloxy)phenyl)-10H-phenoxazine (3a) was obtained as a yellow powder (1.36 g, yield: 67.0%).$^1$H NMR(500MHz, CDCl$_3$): $\delta$(ppm) 8.39(d, $J$=8.5Hz, 1H), 7.86-7.84(m, 1H), 7.63-7.61(m, 1H), 7.54(d, $J$=7.5Hz, 2H), 7.41-7.36(m, 4H), 7.33-7.30(m, 1H), 7.12-7.10(m, 2H), 6.73-6.66(m, 4H), 6.62-6.58(m, 2H), 5.97(dd, $J$=1.0Hz, $J$=1.0Hz, 2H), 5.30(s, 2H).$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm); 159.29, 150.75, 143.93, 142.96, 136.06, 133.78, 133.67, 128.57, 127.93, 126.96, 125.22, 124.52, 123.39, 123.17, 121.74, 120.27, 117.21, 116.32, 115.63, 113.32, 110.57, 70.89; Anal. Calcd. for C$_{32}$H$_{22}$N$_2$O$_3$: C, 79.65; H, 4.60; N, 5.81. Found C, 79.64; H, 4.56; N, 5.77.

Compound 3a (3.02 g, 6.25 mmol) and 10% Pd/C (1.42 g) were added to THF (220 mL), and aqueous ammonium formate (9 mL, 7.63 g, 121.0 mmol) was added. The reaction mixture was heated at 40 °C for 3 h; then, after cooling, the mixture was filtered, and the filtrate was concentrated. It was recrystallized from hexane/ dichloromethane.

2-(benzo[d]oxazol-2-yl)-5-(10H-phenoxazin-10-yl) phenol was obtained as a yellow powder (0.64 g, yield: 87.5%).$^1$H NMR(500MHz, CDCl$_3$): $\delta$(ppm) 11.72(s, 1H), 8.08(d, $J$=2.5Hz, 1H), 7.80-7.79(m, 1H), 7.61-7.59(m, 1H), 7.45-7.42(m, 3H), 7.36(d, $J$=8.5Hz, 1H), 6.73(dd, $J$=2.0Hz, $J$=1.5Hz, 2H), 6.70-6.6.67(m, 2H), 6.65-6.62(m, 2H), 6.03(dd, $J$=1.5Hz, $J$=1.5Hz, 2H).$^{13}$C NMR (125 MHz,
CDCl$_3$: $\delta$ (ppm); 162.20, 160.77, 149.21, 144.02, 139.87, 133.62, 129.59, 125.77, 125.26, 123.31, 121.74, 121.50, 119.66, 119.46, 115.63, 113.57, 110.79, 110.62; Anal. Calcd. for C$_{25}$H$_{16}$N$_2$O$_3$: C, 75.52; H, 4.11; N, 7.14. Found C, 76.59; H, 4.11; N, 7.14.

Al-1

Aluminum isopropoxide (0.30 g, 1.5 mmol) and 2-(benzo[d]oxazol-2-yl)phenol (0.62 g, 2.94 mmol) were dissolved in toluene (10 ml) and then stirred for 30 minutes. A solution of 4-(diphenylamino)phenol (0.39 g, 1.5 mmol) in toluene (10 ml) was added to the mixture and stirred at 60 $^\circ$C for 5 hours. After cooling, the precipitate was filtered, and the filtrate was evaporated. Bis(2-(benzo[d]oxazol-2-yl)phenolato)(4-(diphenylamino)phenolato) aluminum (III) was obtained (0.53 g, yield: 49.6%). $^1$H NMR(500MHz, CDCl$_3$) $\delta$(ppm) 8.10-8.06(m, 2H), 7.64-7.62(m, 1H), 7.55(m, 1H), 7.49-7.38(m, 4H), 7.36-7.33(m, 1H), 7.24-7.19(m, 5H), 7.10-7.07(m, 2H), 7.02-6.94(m, 7H), 6.84-6.77(m, 2H), 6.70-6.66(m, 2H), 6.45(d, $J=8.5$Hz, 1H), 6.28(d, $J=8.5$Hz, 1H); Anal. Calcd. for C$_{25}$H$_{16}$N$_2$O$_3$: C, 74.67; H, 4.27; N, 5.94. Found C, 74.53; H, 4.27; N, 5.95.

Al-2'

Aluminum isopropoxide (0.10 g, 0.5 mmol) and 4-(diphenylamino)phenol (0.39 g, 1.5 mmol) were dissolved in ethanol (30 ml) and then stirred at 85 $^\circ$C for 1 hour. Compound 4a (0.39 g, 1.00 mmol) was added to the mixture and then was stirred and refluxed overnight. After cooling, the precipitate was filtered, and the filtrate was evaporated. Extra ligands were removed by vapor sublimation. Bis(2-(benzo[d]oxazol-2-yl)-5-(10H-phenoxazin-10-yl)phenolato)(4-(diphenylamino)phenolato) aluminum (III) was obtained (0.17 g, yield: 31.0%). $^1$H NMR(500MHz, CDCl$_3$) $\delta$(ppm) 8.5(d, $J=8.5$Hz, 1H), 7.44-7.41(m, 1H), 7.33-7.30(m, 1H), 7.24-7.22(m, 1H), 6.87(dd, $J=2.0$Hz, $J=2.0$Hz, 1H), 6.76(d, $J=0.5$Hz, 1H), 6.69-6.66(m, 4H), 6.51-6.48(m, 2H), 6.12(dd, $J=1.0$Hz, $J=1.0$Hz, 2H); MALDI-TOF-MS (m/z):809.31(Al(PXBOX)$_2$), 826.33(Al(PXBOX)$_2$(OH)).
Zinc acetate (0.25 g, 1.16 mmol) was added to a solution of compound 4a (0.89 g, 2.27 mmol) in ethanol (80 mL). The resulting mixture was stirred at 70 °C overnight. The yellow precipitate was collected by filtration, washed with water and ethanol, and dried in an oven. Bis[2-(benzo[d]oxazol-2-yl)-5-(10H-phenoxazin-10-yl)phenolato]zinc(II) (Zn-1) was obtained as a yellow powder (0.91 g, yield: 93.0%). Purification was achieved by vacuum sublimation. 

\[ \text{Zn-1} \]

\[ \text{H} \text{NMR}(500\text{MHz, CDCl}_3) : \delta(\text{ppm}) \ 8.22(d, J=8.5\text{Hz}, 2\text{H}), 7.68(s, 2\text{H}), 7.60(d, J=8.0\text{Hz}, 2\text{H}), 7.38-7.34(m, 2\text{H}), 7.24-7.21(m, 4\text{H}), 6.69-6.60(m, 14\text{H}), 6.18(d, J=7.5\text{Hz}, 4\text{H}). \]

\[ \text{MALDI-TOF-MS (m/z)}: 846.27; \text{Anal. Calcd. for C}_{50}\text{H}_{30}\text{N}_{4}\text{O}_{6}\text{Zn: C, 70.80; H, 3.57; N, 6.61. Found C, 70.80; H, 3.51; N, 6.61.} \]

Bis(2,4-pentanedionato)magnesium(II) (0.50 g, 0.11 mmol) was added to a solution of compound 4a (0.39 g, 1.00 mmol) in THF (6 mL). The resulting mixture was stirred at 65 °C overnight. The yellow precipitate was collected by filtration, washed with water and ethanol, and dried in an oven to give compound Mg-1 as a yellow powder (0.24 g, yield: 59.0%).

\[ \text{MALDI-TOF-MS (m/z)}: 846.27; \text{Anal. Calcd. for C}_{13}\text{H}_{8}\text{BrNO}_{2}: \text{C, 53.82; H, 2.78; N, 4.83. Found C, 53.86; H, 2.79; N, 4.87.} \]

Lithium hydroxide (0.12 g, 2.8 mmol) was added to a solution of compound 4a (0.72 g, 1.84 mmol) in ethanol (60 mL). The resulting mixture was stirred at 70 °C overnight. The yellow precipitate was collected by filtration, washed with water and ethanol, and dried in an oven to give compound Li-1 as a pale yellow powder (0.70 g, yield: 95.0%). Purification was achieved by vacuum sublimation.

\[ \text{Li-1} \]
Anal. Calcd. for C_{13}H_{8}BrNO_{2}: C, 53.82; H, 2.78; N, 4.83. Found C, 53.86; H, 2.79; N, 4.87.

1b

Prepared as described for compound 1a. (1.21 g, yield: 52.2%) \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 11.5 (1H), 8.16 (d, \(J=2.5\) Hz, 1H), 7.76-7.74 (m, 1H), 7.64-7.62 (m, 1H), 7.52 (dd, \(J=2.5\) Hz, \(J=2.5\) Hz, 1H), 7.43-7.41 (m, 2H), 7.03 (d, \(J=8.5\) Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm); 161.60, 157.71, 149.17, 139.80, 136.21, 129.37, 125.87, 125.28, 119.46, 119.37, 112.19, 111.31, 110.81; Anal. Calcd. for C_{13}H_{8}BrNO_{2}: C, 53.82; H, 2.78; N, 4.83. Found C, 53.86; H, 2.79; N, 4.87.

2b

Prepared as described for compound 2a. 2-(2-(benzyloxy)-5-bromophenyl)benzo[d]oxazole (2b) was obtained as yellow powder (0.94 g, yield: 71.2%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 8.32 (d, \(J=2.5\) Hz, 1H), 7.83-7.81 (m, 1H), 7.59-7.53 (m, 4H), 7.41-7.37 (m, 4H), 7.34-7.31 (m, 1H), 7.0 (d, \(J=8.5\) Hz, 1H), 5.30 (s, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm); 156.48, 150.70, 141.92, 136.30, 135.17, 133.84, 128.57, 127.95, 126.86, 125.29, 124.53, 120.27, 118.86, 115.96, 113.40, 110.57, 71.12; Anal. Calcd. for C_{20}H_{14}BrNO_{2}: C, 63.18; H, 3.71; N, 3.68. Found C, 62.91; H, 3.78; N, 3.77.

3b

Prepared as described for compound 3a. 10-(3-(benzo[d]oxazol-2-yl)-4-(benzyloxy)phenyl)-10H-phenoxazine (3b) was obtained as yellow powder (0.43 g, yield: 60.7%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 8.22 (d, \(J=2.5\) Hz, 1H), 7.84-7.82 (m, 1H), 7.66 (d, \(J=7.0\) Hz, 2H), 7.60-7.58 (m, 1H), 7.49-7.45 (m, 3H), 7.42-7.34 (m, 4H), 6.72 (dd, \(J=2.0\) Hz, \(J=1.5\) Hz, 2H), 6.69-6.66 (m, 2H), 6.64-6.61 (m, 2H), 6.01 (dd, \(J=1.5\) Hz, \(J=1.5\) Hz, 2H), 5.42 (s, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm); 157.12, 150.62, 143.97, 135.22, 134.34, 134.06, 128.61, 127.99, 126.88, 125.27, 124.50, 123.31,
121.47, 120.27, 116.36, 115.49, 113.34, 110.53, 71.15; Anal. Calcd. for C_{32}H_{22}N_2O_3: C, 79.65; H, 4.60; N, 5.81. Found C, 79.47; H, 4.47; N, 5.78.

4b

Prepared as described for compound 4a. 2-(benzo[d]oxazol-2-yl)-4-(10H-phenoxazin-10-yl)phenol was obtained as yellow powder (0.64 g, yield: 87.5%). \( ^1H \) NMR (500 MHz, CDCl_3): \( \delta \) (ppm) 11.72 (s, 1H), 8.08 (d, \( J=2.5 \) Hz, 1H), 7.81-7.79 (m, 1H), 7.61-7.59 (m, 1H), 7.45-7.43 (m, 3H), 7.36 (d, \( J=8.5 \) Hz, 1H), 6.73 (dd, \( J=2.0 \) Hz, \( J=1.5 \) Hz, 2H), 6.70-6.67 (m, 2H), 6.65-6.62 (m, 2H), 6.03 (dd, \( J=1.5 \) Hz, \( J=1.5 \) Hz, 2H). \( ^{13}C \) NMR (125 MHz, CDCl_3): \( \delta \) (ppm); 161.88, 158.46, 149.17, 144.00, 139.82, 136.26, 134.47, 130.44, 125.85, 125.26, 123.31, 121.46, 120.33, 119.45, 115.52, 113.24, 112.79, 110.74; Anal. Calcd. for C_{25}H_{16}N_2O_3: C, 75.52; H, 4.11; N, 7.14. Found C, 76.53; H, 4.06; N, 7.20.

Zn-2

Prepared as described for compound Zn-1. Bis[2-(benzo[d]oxazol-2-yl)-4-(10H-phenoxazin-10-yl)phenol]zinc (II) (Zn-2) was obtained as a yellow powder (0.70 g, yield: 94.9%). \( ^1H \) NMR (500 MHz, CDCl_3): \( \delta \) (ppm) 8.16 (d, \( J=3.0 \) Hz, 2H), 7.62 (d, \( J=8.0 \) Hz, 2H), 7.41-7.39 (m, 6H), 7.33-7.31 (m, 2H), 7.26-7.24 (m, 2H), 6.75-6.68 (m, 14H), 6.18-6.16 (m, 4H). MALDI-TOF-MS (m/z): 848.17

OMe-1

To a stirred mixture of 1a (0.59 g, 1.50 mmol) and K_2CO_3 (0.31 g, 2.28 mmol) in acetone (23 ml) was added dimethyl sulfate (0.21 ml, 2.28 mmol). After stirring overnight at room temperature, concentrated NH_4OH was added to the mixture, which was then stirred for an additional 2 h. The solvent was evaporated under reduced pressure. The residue was extracted in ethyl acetate and dried MgSO_4, and the solvent was evaporated under reduced pressure. After the solvent was removed, the crude product was purified by silica gel column chromatography with hexane/dichloromethane (1/1
by volume). It was then recrystallized from methanol and dichloromethane.

10-(4-(benzo[d]oxazol-2-yl)-3-methoxyphenyl)-10H-phenoxazine (OMe-1) was obtained as a yellow powder (0.49 g, yield: 79.9%). $^1$H NMR (500 MHz, CDCl$_3$) : $\delta$(ppm) 8.38(d, J=8.0Hz, 1H), 7.66-7.64(m, 1H), 7.42-7.40(m, 2H), 7.14(dd, J=2.0Hz, J=1.5Hz, 1H), 7.11(d, J=2.0Hz, 1H), 6.75(dd, J=2.0Hz, J=1.5Hz, 2H), 6.73-6.70 (m,2H), 6.69-6.65(m,2H), 6.08(dd, J=1.5Hz, J=1.5Hz, 2H), 4.04(s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm); 160.76, 160.67, 150.45, 143.93, 143.14, 142.07, 133.77, 133.66, 125.27, 124.50, 123.39, 122.89, 121.77, 120.41, 116.49, 115.67, 114.26, 113.31, 110.57, 56.57; MALDI-TOF-MS (m/z):848.17; 392.08; Anal. Calcd. for C$_{26}$H$_{18}$N$_2$O$_3$: C, 76.83; H,4.46; N, 6.89. Found C, 76.87; H, 4.43; N, 6.86.
Fig. S1 Molecular orbitals for Al complexes Al-1 and Al-2.
Table S1 Calculated energy levels, oscillator strengths \((f)\), and orbital transition analyses for selected lower-lying transitions for the Al complexes, Al-1 and Al-2

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<td>HOMO → LUMO (88%)</td>
<td>LLCT</td>
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<td>(S_1)</td>
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Fig. S2 (a) Emission spectrum and phosphorescence spectrum at 77 K for Al-1 in 2-MeTHF solution. (b) Phosphorescence spectra at 77 K for Al-1 and the ligands of Al-1 in 2-MeTHF solutions. (c) Photoluminescence decay curves for 6wt% Al-1: DPEPO film at 300 K and 5 K.
Fig. S3 Selected frontier orbitals involved in the lower-lying electronic transitions of Zn-1 and Zn-2.

Table S2 Calculated energy levels, oscillator strengths ($f$), and orbital transition analyses for selected lower-lying transitions

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<td>S1</td>
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<td>HOMO $\rightarrow$ LUMO+1</td>
<td>44%</td>
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Fig. S4 TG-DTA data for Al-2' and Zn-1.
Fig. S5 (a) Emission spectrum and phosphorescence spectrum at 77 K for Al-2' in 2-MeTHF solution. (b) Phosphorescence spectra at 77 K for Al-2' and PX-BOX-OH in 2MeTHF solutions.

Fig. S6 Photoluminescence decay curves for a 6wt% Al-2': mCP film at 300 K to 5 K.

Fig. S7 Photoluminescence spectra of 6wt% emitter: mCBP films for Zn-1, Zn-2, and OMe-1.
Fig. S8 Fluorescence and phosphorescence spectra of 6wt% emitter: mCBP films and their transient PL decay at different temperatures: (a, d) Zn-1; (b, e) Zn-2; and (c, f) OMe-1. Red lines represent supporting lines to determine $S_1$ and $T_1$ energies.
Eq. S1

Using PL efficiencies and decay times, we calculated the rate constants for the transitions in Fig. S9 using the following equations.\[^{[17]}\]

\[
\begin{align*}
  k^S_r &= \phi_F k_p \\
  k_{ISC} &= (1 - \phi_F) k_p \\
  k_{RISC} &= \frac{k_p k_d \phi_{TADF}}{k_{ISC} \phi_F} \\
  k^T_{nr} &= k_d - \phi_F k_{RISC}
\end{align*}
\]

- $k^S_r$: radiative decay rate from $S_1$ to $S_0$
- $k^S_{nr}$: non-radiative decay rate from $S_1$ to $S_0$
- $k_p (= 1/\tau_p)$: rate constant of prompt component
- $k_d (= 1/\tau_d)$: rate constant of delayed component

For the materials here, $k^S_{nr} = 0$ at 300K since there was no temperature dependence between 5 K and 300 K for $\phi_F$. 

\[\text{Fig. S9 Energy diagram.}\]
Fig. S10 (a) The $\eta_{\text{ext}}$-current density characteristics of the Al-2 OLED. (b) Luminance-current density-voltage characteristics of the OLED. (c) EL and PL spectra of 6wt%-Al-2 doped in an mCP layer. The OLED is composed of indium-tin-oxide (ITO)/poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (40 nm)/6 ± 1 wt% Al-2': mCP (20 nm)/1,3,5-tris(N-phenyl benzimidazol-2-yl)benzene (TPBi, 55 nm)/LiF (0.8 nm)/Al (80 nm).
Eq. S2

The relationship between internal electroluminescence efficiency ($\eta_{\text{int}}$) and external electroluminescence efficiency ($\eta_{\text{ext}}$) and the theoretical maxima for $\eta_{\text{int}}$ and $\eta_{\text{ext}}$ are given by the following equations:[6]

$$\eta_{\text{ext}} = \eta_{\text{int}} \eta_{\text{out}}$$

$$\eta_{\text{int}} = \eta_{r,S} \phi_F + \{\eta_{r,S}(1 - \phi_F) + \eta_{r,T}\} \times \frac{\phi_{TADF}}{1 - \phi_F}$$

where $\eta_{\text{out}}$ is the light outcoupling efficiency, $\eta_{r,S}$ is the singlet exciton production rate (25%), and $\eta_{r,T}$ is the triplet exciton production rate (75%).

Fig S11. OLED device structures and the molecular structures of the compounds used in the devices.
Fig. S12 Photoluminescence spectra of 6 wt% emitter: mCBP films for Li-1 and Mg-1.

Fig. S13 Fluorescence and phosphorescence spectra of 6 wt% emitter: mCBP films: (a) Li-1 and (b) Mg-1. Red lines represent supporting lines to determine S₁ and T₁ energies.
The spin-orbit coupling constant, $\zeta$, is described as:

$$\zeta_{nl} = \frac{e^2 h^2}{8\pi^2 m^2 c^2 a_0^3} \frac{Z^4}{n^3(l + 1)(l + \frac{1}{2}) l}$$

where $n$ and $l$ are the usual quantum numbers and $Z$ is the atomic number. The heavy atom effect is the dependence on $Z^4$ dependence with modifications to account for screening of the nucleus ($n^3$) and orbital perturbation into the nucleus ($(l + 1)(l + 1/2)$).

The rate constant of decay should be proportional to the square of the spin-orbit coupling constant:

$$k_d \propto \zeta_{nl}^2$$

Thus, the term $\log k + \log n^6$ was used for quantifying the heavy atom effect.

According to the method from a previous report, we plotted $\log k + \log n^6$ vs. $\log Z$ for the rate constants and estimated the extent of the spin-orbit coupling from the slope (Figure S14). In the previous work, Mg and Zn were put in the same group, and the slope was 3.38. In the present study, a slope of 3.2 was obtained for $k_d$, which encompasses the important processes in these TADF materials, indicating the presence of a heavy atom effect.

![Figure S14](image-url)