Electronic Supplementary Information (ESI)

Blue thermally activated delayed fluorescence emitters incorporating acridan analogues with heavy group 14 elements for high-efficiency doped and non-doped OLEDs

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1. Materials, Synthesis, and Characterization

All reagents and anhydrous solvents were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or FUJIFILM Wako Pure Chemical Corp., and were used without further purification unless otherwise noted. \(N,N\)-Bis(2-bromo-4-methylphenyl)benzylamine\(^1\) and 3-bromo-10-(2,4,6-triisopropylphenyl)-dibenzo\([b,e]\)[1,4]thiaborin\(^2\) were prepared according to the literature procedures. 2,3,6,7,10,11-Hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN) was donated by the Nippon Soda Co., Ltd. and purified by vacuum sublimation before use. Other OLED materials were purchased from E-Ray Optoelectronic Technology Co., Ltd. and were used without further purification. Final products 1–4 were purified by temperature-gradient vacuum sublimation to provide highly pure materials for photophysical measurements and device fabrications. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz, for \(^1\)H and 100 MHz for \(^{13}\)C, respectively). Chemical shifts of \(^1\)H and \(^{13}\)C NMR signals were quoted to tetramethylsilane (\(\delta = 0.00 \text{ ppm}\)) and CDCl\(_3\) (\(\delta = 77.00 \text{ ppm}\)), respectively, as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as matrices. Elemental analyses were carried out with a Yanaco MT-5 analyzer. Thermogravimetric analyses (TGA) were performed using a Hitachi High-Tech Science TG/DTA7300 analyzer at a heating rate of 10 °C min\(^{-1}\) under N\(_2\) and 5% weight-loss temperatures (\(T_d\)) of 1–4 were determined.

\[\text{Bn-MPASi} \text{ (85\%)} \]
\[\text{MPASi} \text{ (39\%)} \]

\(N\)-Benzyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrodibenz[\(b,e\)][1,4]azasiline (Bn-MPASi): To a stirred solution of \(N,N\)-bis(2-bromo-4-methylphenyl)benzylamine (2.67 g, 6.00 mmol) in anhydrous diethyl ether (30 mL) was added dropwise \(n\)-butyllithium in hexane (1.51 M, 8.4 mL, 12.7 mmol) at 0 °C under N\(_2\). The mixture was stirred at 0 °C for 1 h, and then, dichlorodiphenylsilane (1.4 mL, 6.75 mmol) was added dropwise. The reaction mixture was stirred at 35 °C for 2 h and then cooled to room temperature. After the addition of water, the product was extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/CH\(_2\)Cl\(_2\) = 4:1, v/v). After removal of
the solvents by evaporation, the resulting solid was washed with MeOH to afford Bn-MPASi as a white solid (yield = 2.37 g, 85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58–7.56 (m, 4H), 7.44–7.34 (m, 6H), 7.32–7.27 (m, 5H), 7.20 (d, $J = 6.8$ Hz, 2H), 7.06 (dd, $J = 8.8$, 1.6 Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 5.17 (s, 2H), 2.23 (s, 6H). MS (MALDI-TOF): $m/z$ calcd 467.21 [$M^+$]; found 467.30.

2,8-Dimethyl-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azasiline (MPASi): A suspension of Bn-MPASi (1.87 g, 4.00 mmol) and 5% Pd/C (427 mg) in a mixed solvent of CH$_2$Cl$_2$ (10 mL) and AcOH (10 mL) was vigorously stirred under H$_2$ atmosphere at room temperature for 24 h. After the reaction mixture was filtered through a Celite® pad, the filtrate was neutralized with an aqueous solution of NaHCO$_3$. The product was extracted with CH$_2$Cl$_2$, and then washed with brine and dried over anhydrous Na$_2$SO$_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/CH$_2$Cl$_2$ = 2:1, v/v). After removal of the solvents by evaporation, the resulting solid was washed with MeOH to afford MPASi as a white solid (yield = 581 mg, 39%). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 9.23 (s, 1H), 7.48–7.43 (m, 4H), 7.41–7.36 (m, 6H), 7.19 (s, 2H), 7.15 (dd, $J = 8.4$, 1.6 Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 2.19 (s, 6H). MS (MALDI-TOF): $m/z$ calcd 377.16 [$M^+$]; found 377.04.

5'-Benzyl-2',8'-dimethyl-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline] (Bn-MFASi): 5,5-Dichloro-5'H-dibenzo[b,d]silole was synthesized according to the literature.$^3$ To a stirred solution of 2,2'-dibromobiphenyl (2.50 g, 8.00 mmol) in anhydrous diethyl ether (20 mL) was added dropwise n-buthyllithium in hexane (1.6 M, 10.3 mL, 16.5 mmol) at $-78$ °C under N$_2$. The mixture was stirred at the same temperature for 1 h, and then, stirred at 0 °C for 1 h. The dilithiated intermediate was added dropwise to a stirred solution of tetrachlorosilane (4.5 mL, 40 mmol) precooled to $-78$ °C in anhydrous THF (40 mL). The reaction mixture was
stirred at the same temperature for 1 h, and allowed to gradually warm to room temperature. After the solvent was removed in vacuo, anhydrous toluene (20 mL) was added and the suspension was vigorously stirred. The inorganic salts were removed by filtration and solvent was removed in vacuo. The crude product was used for the next reaction without purification.

To a stirred solution of N,N-bis(2-bromo-4-methylphenyl)benzylamine (3.21 g, 7.20 mmol) in anhydrous diethyl ether (40 mL) was added dropwise n-buthyllithium in hexane (1.6 M, 9.5 mL, 15.2 mmol) at 0 °C under N₂. The mixture was stirred at 0 °C for 1 h, and then, 5,5-dichloro-5'H-dibenzo[b,d]silole (8.00 mmol, if pure) in anhydrous toluene (12 mL) was added dropwise. The reaction mixture was stirred at 35 °C for 2 h and then cooled to room temperature. After the addition of water, the product was extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/toluene = 4:1, v/v) to afford Bn-MFASi as a white solid (yield = 2.94 g, 88%). ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 8.0 Hz, 4H), 7.54–7.48 (m, 4H), 7.43–7.32 (m, 5H), 7.24 (d, J = 7.2 Hz, 2H), 7.08 (dd, J = 8.4, 2.0 Hz, 2H), 6.98 (d, J = 2.0 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.35 (s, 2H), 2.11 (s, 6H). MS (MALDI-TOF): m/z calcd 465.19 [M]+; found 465.36.

2',8'-Dimethyl-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline] (MFASi): A suspension of Bn-MFASi (1.40 g, 3.00 mmol) and 5% Pd/C (321 mg) in a mixed solvent of CH₂Cl₂ (7.5 mL) and AcOH (7.5 mL) was vigorously stirred under H₂ atmosphere at room temperature for 15 h. After the reaction mixture was filtered through a Celite® pad, the filtrate was neutralized with an aqueous solution of NaHCO₃. The product was extracted with CH₂Cl₂, and then washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 2:1, v/v) to afford MFASi as a white solid (yield = 322 mg, 29%). ¹H NMR (400 MHz, DMSO-d₆): δ 9.50 (s, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.51 (dd, J = 7.6, 7.6 Hz, 2H), 7.34 (d, J = 6.4 Hz, 2H), 7.23 (dd, J = 7.2, 7.2 Hz, 2H), 7.17 (dd, J = 8.8, 2.0 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 1.6 Hz, 2H), 2.05 (s, 6H). MS (MALDI-TOF): m/z calcd 375.14 [M]+; found 375.11.
**N-Benzyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azagermine** (Bn-MPAGe): To a stirred solution of \( N,N\)-bis(2-bromo-4-methylphenyl)benzylamine (2.23 g, 5.00 mmol) in anhydrous diethyl ether (25 mL) was added dropwise \( n\)-butyllithium in hexane (1.6 M, 6.6 mL, 10.6 mmol) at 0 °C under N\(_2\). The mixture was stirred at 0 °C for 1 h, and then, dichlorodiphenylgermane (1.65 g, 5.55 mmol) was added dropwise. The reaction mixture was stirred at 35 °C for 2 h and then cooled to room temperature. After the addition of water, the product was extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/CH\(_2\)Cl\(_2\) = 4:1, v/v). After removal of the solvents by evaporation, the resulting solid was washed with MeOH to afford Bn-MPAGe as a white solid (yield = 2.11 g, 82%).\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.56–7.53 (m, 4H), 7.42–7.36 (m, 6H), 7.32–7.27 (m, 5H), 7.14 (d, \( J = 7.6 \) Hz, 2H), 7.03 (dd, \( J = 8.4, 2.0 \) Hz, 2H), 6.90 (d, \( J = 8.8 \) Hz, 2H), 5.12 (s, 2H), 2.23 (s, 6H). MS (MALDI-TOF): \( m/z \) calcd 512.15 \([M]^+\); found 512.37.

**2,8-Dimethyl-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azagermine** (MPAGe): A suspension of Bn-MPAGe (1.54 g, 3.00 mmol) and 5% Pd/C (320 mg) in a mixed solvent of CH\(_2\)Cl\(_2\) (7.5 mL) and AcOH (7.5 mL) was vigorously stirred under H\(_2\) atmosphere at room temperature for 24 h. After the reaction mixture was filtered through a Celite\textsuperscript{®} pad, the filtrate was neutralized with an aqueous solution of NaHCO\(_3\). The product was extracted with CH\(_2\)Cl\(_2\), and then washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/CH\(_2\)Cl\(_2\) = 2:1, v/v). After removal of the solvents by evaporation, the resulting solid was washed with MeOH to afford MPAGe as a white solid (yield = 319 mg, 25%).\(^1\)H NMR (400 MHz, DMSO-\( d_6\)): \( \delta \) 8.99 (s, 1H), 7.47–7.43 (m, 4H), 7.42–7.38 (m, 6H), 7.17 (d, \( J = 1.2 \) Hz, 2H), 7.10 (dd, \( J = 8.4, 2.4 \) Hz, 2H), 6.96 (d, \( J = 8.4 \) Hz, 2H), 2.19 (s, 6H). MS (MALDI-TOF): \( m/z \) calcd 423.10 \([M]^+\); found 423.10.
Compound 1 (MPASi-BS): A mixture of MPASi (453 mg, 1.20 mmol), Br-BS (573 mg, 1.20 mmol), Pd$_2$(dba)$_3$ (22 mg, 0.024 mmol), P(t-Bu)$_3$H·BF$_4$ (28 mg, 0.097 mmol), and sodium tert-butoxide (233 mg, 2.43 mmol) in anhydrous toluene (12 mL) was stirred at 100 °C for 14 h under N$_2$. After addition of aqueous solution of NH$_4$Cl, the product was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/toluene = 5:1, v/v) to afford 1 as a yellow solid (yield = 828 mg, 89%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93–7.90 (m, 2H), 7.70 (d, $J$ = 7.6 Hz, 1H), 7.60–7.56 (m, 5 H), 7.45 (d, $J$ = 1.6 Hz, 1H), 7.39–7.28 (m, 9H), 7.07 (s, 2H), 7.06–7.01 (m, 3H), 6.67 (d, $J$ = 8.4 Hz, 1H), 2.99 (sept, $J$ = 6.8 Hz, 1H), 2.29 (sept, $J$ = 6.8 Hz, 2H), 2.25 (s, 6H), 1.35 (d, $J$ = 6.8 Hz, 6H), 1.01 (d, $J$ = 6.8 Hz, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.99, 148.32, 148.03, 147.46, 145.60, 143.26, 142.36, 140.20, 136.15, 135.90, 134.21, 131.82, 131.17, 130.86, 129.61, 127.84, 124.91, 124.40, 122.59, 121.53, 121.30, 120.21, 120.03, 35.37, 34.27, 24.31, 24.27, 24.20, 20.54. MS (MALDI-TOF): calcd 773.37 [M]+; found 773.00. Anal. calcd (%) for C$_{53}$H$_{52}$BNSSi: C 82.25, H 6.77, N 1.81; found: C 81.78, H 6.73, N 1.83. $T_d$ = 368 °C.

Compound 2 (MFASi-BS): A mixture of MFASi (376 mg, 1.00 mmol), Br-BS (478 mg, 1.00 mmol), Pd$_2$(dba)$_3$ (18 mg, 0.020 mmol), P(t-Bu)$_3$H·BF$_4$ (24 mg, 0.081 mmol), and sodium tert-butoxide (192 mg, 2.00 mmol) in anhydrous toluene (10 mL) was stirred at 100 °C for 17 h under N$_2$. After addition of aqueous solution of NH$_4$Cl, the product was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/toluene = 4:1, v/v) to afford 2 as a yellow solid (yield = 589 mg, 76%). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.08 (d, $J$ = 8.0 Hz, 1H), 7.97 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.93 (d, $J$ = 8.0 Hz, 2H), 7.74 (d, $J$ = 8.0 Hz, 2H), 7.65 (d, $J$ = 2.0 Hz, 1H), 7.61 (ddd, $J$ = 8.0, 8.0, 1.2 Hz, 1H), 7.49 (ddd, $J$ = 8.0, 8.0, 1.6 Hz, 2H), 7.42 (d, $J$ = 7.2 Hz, 2H), 7.34 (ddd, $J$ = 8.0, 8.0, 1.2 Hz, 1H), 7.22–7.18 (m, 3H), 7.10 (s, 2H), 7.07–7.04 (m, 4H), 6.70 (m, 2H), 3.00 (sept, $J$ = 6.8 Hz, 1H), 2.35 (sept, $J$ = 6.8 Hz, 2H), 2.13 (s, 6H), 1.37 (d, $J$ = 6.8 Hz, 6H), 1.05 (d, $J$ = 6.8 Hz, 6H), 1.05 (d, $J$ = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$):
Compound 3 (MPAGE-Bs): A mixture of MPAGE (422 mg, 1.00 mmol), Br-Bs (477 mg, 1.20 mmol), Pd₂dba₃ (19 mg, 0.021 mmol), P(t-Bu)₃H·BF₄ (24 mg, 0.082 mmol), and sodium tert-butoxide (194 mg, 2.01 mmol) in anhydrous toluene (10 mL) was stirred at 100 °C for 16 h under N₂. After addition of aqueous solution of NH₄Cl, the product was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/toluene = 4:1, v/v) to afford 3 as a white solid (yield = 573 mg, 70%). H NMR (400 MHz, CDCl₃): δ 7.79 (dd, J = 8.0, 1.6 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.48 (ddd, J = 8.0, 8.0, 1.6 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.41–7.38 (m, 6H), 7.31 (d, J = 2.0 Hz, 2H), 7.24–7.17 (m, 9H), 7.00 (s, 2H), 6.93 (d, J = 2.4 Hz, 1H), 6.64 (dd, J = 8.8, 2.4 Hz, 1H), 2.94 (sept, J = 6.8 Hz, 1H), 2.33 (s, 6H), 2.24 (sept, J = 6.8 Hz, 2H), 1.32 (d, J = 7.2 Hz, 6H), 0.96 (d, J = 6.8 Hz, 6H), 0.95 (d, J = 6.8 Hz, 6H). C NMR (100 MHz, CDCl₃): δ 150.36, 149.95, 147.80, 145.60, 145.08, 143.25, 141.18, 139.73, 135.66, 135.63, 135.20, 133.53, 131.00, 130.53, 129.25, 128.09, 127.04, 124.64, 123.91, 119.72, 112.88, 109.19, 34.97, 34.26, 24.42, 24.36, 24.20, 20.95. MS (MALDI-TOF): calcd 819.31 [M]+; found 819.10.

Compound 4 (MCz-Bs): A mixture of MCz (493 mg, 2.21 mmol), Br-Bs (955 mg, 2.00 mmol), Pd₂dba₃ (37 mg, 0.040 mmol), P(t-Bu)₃H·BF₄ (46 mg, 0.16 mmol), and sodium tert-butoxide (302 mg, 3.96 mmol) in anhydrous toluene (20 mL) was stirred at 100 °C for 6 h under N₂. After addition of aqueous solution of NH₄Cl, the product was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/toluene = 5:1, v/v) to afford 4 as a white solid (yield = 712 mg, 58%). H NMR (400 MHz, CDCl₃): δ 8.02 (dd, J = 8.0, 1.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.77–7.75 (m, 3H), 7.63 (ddd, J = 8.0, 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 2.0 Hz, 1H), 7.36 (ddd, J = 8.0, 8.0, 0.8 Hz, 1H), 7.10 (s, 2H), 6.91 (s, 2H), 3.00 (sept, J = 6.8 Hz, 1H), 2.47 (s, 6H), 2.28 (sept, J = 6.8 Hz, 2H), 1.86 (s, 6H), 1.36 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.8 Hz, 2H).
$= 6.8 \text{ Hz}, 6\text{H}), 0.99 (d, J = 6.8 \text{ Hz}, 6\text{H}). ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 149.95, 148.64, 145.62, 143.48, 143.23, 140.40, 140.28, 139.40, 137.57, 134.70, 132.30, 130.29, 129.25, 127.39, 127.22, 125.07, 124.76, 124.34, 121.20, 120.18, 117.85, 35.61, 34.28, 24.19, 24.12, 24.08, 21.10, 19.30. \text{ MS (MALDI-TOF): calcd 619.34 } [M]^+\text{; found 619.24. Anal. calcd (\%) for C}_{43}\text{H}_{46}\text{BNS: C 83.34, H 7.48, N 2.26; found: C 83.39, H 7.41, N 2.28. } T_d = 343 \text{ °C.}$

**Fig. S1** TGA thermograms of 1–4 at a heating rate of 10 °C min$^{-1}$ under N$_2$. 
**Fig. S2** $^1$H and $^{13}$C NMR spectra of 1 in CDCl$_3$. 
Fig. S3 $^1$H and $^{13}$C NMR spectra of 2 in CDCl$_3$. 

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**Fig. S4** $^1$H and $^{13}$C NMR spectra of 3 in CDCl$_3$. 
Fig. S5 $^1$H and $^{13}$C NMR spectra of 4 in CDCl$_3$. 
2. X-ray Crystallographic Analysis

Single crystal X-ray diffraction measurements were performed on a Rigaku AFC-10 diffractometer with a Saturn724+ CCD detector for 1 and 4, and a Rigaku XtaLAB diffractometer with a HyPix-6000 detector for 2 and 3. The diffraction data were collected using Mo-Kα radiation (λ = 0.71073 Å) monochromated with multi-layer mirror. The structures were solved by direct methods (SHELXT-20164) and refined by the full-matrix least-squares on $F^2$ (SHELXL-20164). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions.

Crystallographic data for 1: The measurement was performed at 163 K. Total 46622 reflections were collected, among which 10032 reflections were independent ($R_{int} = 0.0892$). The crystal data: Formula C$_{53}$H$_{52}$BNSSi; FW = 773.91, crystal size 0.13 × 0.08 × 0.05 mm, Monoclinic, $P2_1/n$ (#14), $a = 16.28(3)$ Å, $b = 8.916(15)$ Å, $c = 30.47(5)$ Å, $α = γ = 90^°$, $β = 97.92(3)^°$, $V = 4381(13)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.173$ g cm$^{-3}$, $R_1 = 0.0681$ ($I > 2σ(I)$), $wR_2 = 0.1773$ (all data), GOF = 1.068. Two isopropyl groups were disordered. The crystal data is deposited in The Cambridge Crystallographic Data Centre (CCDC number: 1948037).

Crystallographic data for 2: The measurement was performed at 173 K. Total 50514 reflections were collected, among which 10707 reflections were independent ($R_{int} = 0.0343$). The crystal data: Formula C$_{53}$H$_{50}$BNSSi·C$_4$H$_8$O$_2$; FW = 860.00, crystal size 0.16 × 0.15 × 0.06 mm, Monoclinic, $P2_1/c$ (#14), $a = 18.0660(3)$ Å, $b = 13.8091(3)$ Å, $c = 19.3607(3)$ Å, $α = γ = 90^°$, $β = 99.953(2)^°$, $V = 4757.32(15)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.201$ g cm$^{-3}$, $R_1 = 0.0610$ ($I > 2σ(I)$), $wR_2 = 0.1803$ (all data), GOF = 1.039. One AcOEt molecule used as solvent were contained in an asymmetric unit of the crystal lattice. One isopropyl group was disordered. The crystal data is deposited in The Cambridge Crystallographic Data Centre (CCDC number: 1948038).

Crystallographic data for 3: The measurement was performed at 173 K. Total 90630 reflections were collected, among which 10418 reflections were independent ($R_{int} = 0.0431$). The crystal data: Formula C$_{53}$H$_{52}$BNSGe·C$_2$H$_3$N; FW = 859.47, crystal size 0.25 × 0.13 × 0.08 mm, Monoclinic, $P2_1/n$ (#14), $a = 14.0919(2)$ Å, $b = 9.10970(10)$ Å, $c = 36.2632(6)$ Å, $α = γ = 90^°$, $β = 100.447(2)^°$, $V = 4578.04(12)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.247$ g cm$^{-3}$, $R_1 = 0.0339$ ($I > 2σ(I)$), $wR_2 = 0.0993$ (all data), GOF = 1.086. One acetonitrile molecule used as solvent were contained in an asymmetric unit of the crystal lattice. The crystal data is deposited in The Cambridge Crystallographic Data Centre (CCDC number: 1948039).
Crystallographic data for 4: The measurement was performed at 163 K. Total 17959 reflections were collected, among which 7985 reflections were independent ($R_{int} = 0.0657$). The crystal data: Formula C$_{43}$H$_{46}$BNS; FW = 619.68, crystal size 0.15 × 0.05 × 0.03 mm, Triclinic, $P$–$1$ (#2), $a = 10.103(8)$ Å, $b = 12.791(10)$ Å, $c = 13.778(12)$ Å, $α = 84.552(16)^\circ$, $β = 86.292(18)^\circ$, $γ = 83.85(2)^\circ$, $V = 1760(2)$ Å$^3$, $Z = 2$, $D_{calc} = 1.170$ g cm$^{-3}$, $R_1 = 0.0800$ ($I > 2σ(I)$), $WR_2 = 0.3052$ (all data), GOF = 1.065. The crystal data is deposited in The Cambridge Crystallographic Data Centre (CCDC number: 1948040).
3. **Electrochemical Analysis**

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using an ALS CHI 612E electrochemical analyzer and a three-electrode cell equipped with Pt working and counter electrodes and an Ag/AgNO$_3$ reference electrode. The measurements were carried out for CH$_2$Cl$_2$ solutions of 1–5 (1 mM) at a scanning rate of 50 mV s$^{-1}$. Tetrabutylammonium perchlorate ($n$-Bu$_4$NClO$_4$) was used as a supporting electrolyte with a concentration of 0.1 M. The redox potentials were calibrated with ferrocene as an internal standard.

![Cyclic voltammograms of 1–5 in CH$_2$Cl$_2$ measured at a scanning rate of 50 mV s$^{-1}$](image)

**Fig. S6** Cyclic voltammograms of 1–5 in CH$_2$Cl$_2$ measured at a scanning rate of 50 mV s$^{-1}$.

![Differential pulse voltammograms of 1–5 in CH$_2$Cl$_2$.](image)

**Fig. S7** Differential pulse voltammograms of 1–5 in CH$_2$Cl$_2$. 

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4. Photophysical Properties

UV–vis absorption spectra were measured with a Jasco V-670 spectrometer. Fluorescence and phosphorescence spectra were measured with a Jasco FP-8600 spectrophotometer. Absolute photoluminescence quantum yields (Φ_{PL}) were determined with a Jasco ILF-835 integrating sphere system. The transient PL decay measurements were performed using a Quantaurus-Tau C11367 under N2. Photophysical properties of 1–4 in toluene solutions were measured by using deoxygenated spectral grade solvents with the concentration of 2–5 × 10^{-5} M. Pure neat films for the optical measurements were deposited under high vacuum (< 1 × 10^{-4} Pa) onto quartz substrates. The optical energy gaps (E_g) were determined from the high-energy onset position of the absorption spectra of pure neat films. The ionization potentials (IP) were determined from the photoelectron yield spectra of pure neat films. The electron affinities (EA) were estimated by subtracting E_g from the measured IP. The 50 wt% -doped films for the optical measurements were co-deposited with PPF as a host material under high vacuum (< 1 × 10^{-4} Pa) onto quartz substrates. The singlet and triplet excitation energies (E_S and E_T) of 1–4 were estimated from the high-energy onset positions of the fluorescence and phosphorescence spectra of the doped films. The phosphorescence spectra of MPASi, MFASi, MPAGE, MCz, and Br-BS were measured in frozen toluene solutions at 77 K. The phosphorescence spectrum of Br-BS in the film was measured using 50 wt%-doped film in PPF prepared by drop-casting. The rate constants for the TADF decay process of 1–4 were calculated according to the literature.\(^5\)
Fig. S8 Absorption and excitation spectra (for QE and QA) of (a) 1, (b) 2, (c) 3, and (d) 4 in toluene solutions.

Fig. S9 Transient PL decay curves (for QE) of (a) 1, (b) 2, (c) 3, and (d) 4 in deoxygenated toluene solutions at 300 K.
### Table S1 Photophysical data for 1–4 in toluene solutions

|   | $\lambda_{PL}$ [nm] | $E_{\text{FWHM}}$ [eV] | $\lambda_{\text{FWHM}}$ [nm] | $\Phi_{PL}$ [%] | $\tau_p$ [ns] | $\tau_d$ [$\mu$s] |
|---|---------------------|------------------------|-----------------------|-----------------|---------------|------------------|
| 1 | 409, 478            | 0.36$^a$               | 68$^a$                 | 46$^b$          | 1.4$^c$      | 0.54$^c$         |
| 2 | 410, 472            | 0.38$^a$               | 69$^a$                 | 27$^b$          | 5.3$^c$      | 4.3$^c$          |
| 3 | 403, 482            | 0.37$^a$               | 70$^a$                 | 42$^b$          | 1.9$^c$      | 0.53$^c$         |
| 4 | 458                 | 0.38                   | 67                     | 22              | 0.39         | 15.7             |

$^a$Full width at half-maximum of the PL for QE. $^b$PL quantum yield evaluated from overall emissions of QA and QE. $^c$Emission lifetime for QE.

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Fig. S10 UV–vis absorption spectra of (a) 1, (b) 2, (c) 3, and (d) 4 in various solvents.
Fig. S11 PL spectra of (a) 2, (b) 3, and (c) 4 in various solvents.

Table S2 Summary of the maximum PL wavelength of 1–4 in different solvents

|     | cyclohexane | toluene | AcOEt | CH$_2$Cl$_2$ |
|-----|-------------|---------|-------|-------------|
| 1   | 403         | 409, 478| 410, 517| 419, 540    |
| 2   | 397         | 410, 472| 405, 512| 413, 535    |
| 3   | 403         | 403, 482| 407, 521| 416, 540    |
| 4   | 419         | 458     | 498    | 518         |
Fig. S12 Photoelectron yield spectra of 1–4 in neat films.

Table S3 Photophysical data for 1–4 in neat films

|       | $\lambda_{\text{abs}}$ (onset) [nm] | $E_g$ [eV] | $E_{\text{IP}}$ [eV] | $E_{\text{EA}}$ [eV] |
|-------|----------------------------------|-----------|-----------------|-----------------|
| 1     | 440                              | 2.82      | 5.78            | 2.96            |
| 2     | 438                              | 2.83      | 5.77            | 2.94            |
| 3     | 391                              | 3.17      | 5.87            | 2.70            |
| 4     | 429                              | 2.89      | 5.68            | 2.79            |

Fig. S13 Fluorescence (300 K) and phosphorescence spectra of (a) 1, (b) 2, (c) 3, and (d) 4 in 50 wt%-doped films.
Fig. S14 (a) Phosphorescence spectra of donor and acceptor units in frozen toluene solutions at 77 K. (b) Phosphorescence spectra of 1–4 and Br-BS in 50 wt%-doped films at 77 K.

Table S4 Excitation energies for the $S_1$ and $T_1$ states and $S_1$–$T_1$ energy splittings

|        | 1$^d$ | 2$^d$ | 3$^d$ | 4$^d$ | MPASI$^e$ | MFASI$^e$ | MPAGe$^e$ | MCz$^e$ | Br-BS$^e$ |
|--------|-------|-------|-------|-------|-----------|-----------|-----------|---------|----------|
| $E_S$$^a$ [eV] | 2.85  | 2.82  | 2.92  | 2.87  | -         | -         | -         | -       | -        |
| $E_T$$^b$ [eV] | 2.77  | 2.76  | 2.81  | 2.76  | 3.01      | 2.78      | 3.07      | 3.04    | 2.92     |
| $\Delta E_{ST}$$^c$ [eV] | 0.08  | 0.06  | 0.11  | 0.11  | -         | -         | -         | -       | -        |

$^a$The lowest singlet excitation energy estimated from the onset energy of fluorescence spectrum at 300 K. $^b$The lowest triplet excitation energy estimated from the onset energy of phosphorescence spectrum at 77 K. $^c\Delta E_{ST} = E_S - E_T$. $^d$Measured in the 50 wt%-doped films in PPF. $^e$Measured in the frozen toluene solution.
5. Computational Methods

Geometry optimization for 1–5 in the S_0 state were performed using the B3LYP functional with the 6-31G(d) basis set in the gas phase, implemented in the Gaussian 16 program package. The transition-state (TS) geometries were optimized using TS keyword. It was confirmed that the transition states show only one negative imaginary frequency and the optimized structures displaced in the direction of negative frequency from the TS geometries are identical to the QA or QE geometries. The population ratios between QE and QA were estimated by Boltzmann distribution as follows,

\[
[Q\!A]\text{(%)} = \frac{2 \times \exp\left(-\frac{\Delta G_{QA}}{k_b T}\right)}{2 \times \exp\left(-\frac{\Delta G_{QA}}{k_b T}\right) + \exp\left(-\frac{\Delta G_{QE1}}{k_b T}\right) + \exp\left(-\frac{\Delta G_{QE2}}{k_b T}\right)}
\]

\[
[Q\!E]\text{(%)} = \frac{\exp\left(-\frac{\Delta G_{QE1}}{k_b T}\right) + \exp\left(-\frac{\Delta G_{QE2}}{k_b T}\right)}{2 \times \exp\left(-\frac{\Delta G_{QA}}{k_b T}\right) + \exp\left(-\frac{\Delta G_{QE1}}{k_b T}\right) + \exp\left(-\frac{\Delta G_{QE2}}{k_b T}\right)}
\]

where \(\Delta G\) are the relative Gibbs free energy changes, \(k_b\) is the Boltzmann constant, and \(T\) is the temperature (298 K). The population ratios were calculated considering that there are two enantiomeric isomers in QA for the rotation of donor and acceptor units.

The geometries of the S_1 and T_1 states were optimized using the TD-DFT method at the B3LYP/6-31G(d) level in the gas phase. The singlet and triplet excitation energies were calculated by TD-DFT calculations using the optimally tuned range-separated functional (LC-\(\omega\)PBE) with the 6-31+G(d) basis set. The optimal range-separation parameter \(\omega\) was obtained by minimizing the following equation,

\[
J^2 = \sum_{i=0}^{1} [\varepsilon_{HOMO}(N + i) + IP(N + i)]^2
\]

where \(\varepsilon_{HOMO}\) is the energy of the HOMO and \(IP\) is the ionization potential for the \(N\)-electron system. For the optimization of the \(\omega\) value, the single-point calculations based on the S_0 geometries optimized at B3LYP/6-31G(d) level were carried out for QE and QA of 1. The optimal \(\omega\) values of 0.15 and 0.14 were used in the TD-DFT LC-\(\omega\)PBE calculations for QE of 1–3 and 4, and QA of 1–3, respectively.
Fig. S15 Kohn–Sham molecular orbitals of 2–4 in the $S_0$ states and their energy levels, calculated at the B3LYP/6-31G(d) level.

Fig. S16 $J^2$ values as a function of the range-separation parameter $\omega$ for QE and QA conformers of 1 calculated at the LC-$\omega$PBE/6-31+G(d) level.
**Fig. S17** The singlet excitation wavelengths and oscillator strengths \((f)\), and absorption spectra calculated at the LC-\(\omega\)PBE/6-31+G(d) level in the \(S_0\) optimized geometries. \(H\rightarrow n \rightarrow L+m\) represents the HOMO–\(n\) to LUMO+\(m\) transitions. The values in parentheses imply the weights of transition configurations.

|   | \(\text{QE}\) | \(\text{QA}\) |
|---|---|---|
| 1 | ![HOMO](image1) | ![LUMO](image2) | ![HOMO-1](image3) | ![HOMO](image4) | ![LUMO](image5) |
| 2 | ![HOMO](image6) | ![LUMO](image7) | ![HOMO-1](image8) | ![HOMO](image9) | ![LUMO](image10) |
| 3 | ![HOMO](image11) | ![LUMO](image12) | ![HOMO-1](image13) | ![HOMO](image14) | ![LUMO](image15) |
| 4 | ![HOMO](image16) | ![LUMO](image17) |

**Fig. S18** Kohn–Sham molecular orbitals of 1–4 most involved in the vertical excitations for the \(S_1\) states, calculated at the LC-\(\omega\)PBE/6-31+G(d) level in the optimized \(S_0\) geometries.
### Table S5 TD-DFT calculation results in the optimized $S_1$ and $T_1$ geometries

| state | $E$ [eV] | $\lambda$ [eV] | $E_S, E_T$ [eV] | $f$ [%] | main configuration | $\Delta E_{S1-T1}$ [meV] | $\Delta E_{S1-T1}$ [meV] |
|-------|-----------|-----------------|-----------------|--------|-------------------|---------------------|---------------------|
| 1     | S$_1$     | 2.640           | 0.147           | 2.786  | 0.0001            | $H \rightarrow L$   | 89                  |
|       | T$_1$     | 2.604           | 0.145           | 2.749  | 0.0000            | $H-1 \rightarrow L$ | 79                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 16                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 75                  |
|       |           |                 |                 |        |                   | $H-1 \rightarrow L$ | 17                  |
| 2     | S$_1$     | 2.665           | 0.153           | 2.818  | 0.0001            | $H \rightarrow L$   | 89                  |
|       | T$_1$     | 2.605           | 0.152           | 2.757  | 0.0000            | $H-2 \rightarrow L$ | 90                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 61                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 49                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 84                  |
| 3     | S$_1$     | 2.619           | 0.120           | 2.739  | 0.0001            | $H \rightarrow L$   | 89                  |
|       | T$_1$     | 2.498           | 0.095           | 2.593  | 0.0000            | $H-1 \rightarrow L$ | 97                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 146                 |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 511                 |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 78                  |
| 4     | S$_1$     | 2.729           | 0.137           | 2.866  | 0.0000            | $H \rightarrow L$   | 89                  |
|       | T$_1$     | 2.617           | 0.137           | 2.754  | 0.0000            | $H-2 \rightarrow L$ | 93                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 112                 |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 99                  |
|       |           |                 |                 |        |                   | $H \rightarrow L$   | 88                  |

The excitation energies ($E$), relaxation energies ($\lambda$), the energy levels of the excited states ($E_S$ and $E_T$), $f$, transition configurations, and adiabatic $\Delta E_{ST}$ of 1–4 calculated at the LC-ωPBE/6-31+G(d) level in the $S_1$ and $T_1$ optimized geometries. $E_S$ ($E_T$) = $E + \lambda$.

$H-n \rightarrow L+m$ represents the HOMO−$n$ to LUMO+$m$ transition.
6. OLED Fabrication and Evaluation

Indium tin oxide-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropanol. They were then treated with UV–ozone treatment for 30 min, before being loaded into a vacuum evaporation system. The organic layers were thermally evaporated on the substrates under vacuum (< $1 \times 10^{-4}$ Pa) with an evaporation rate of < 1 Å s$^{-1}$. All of the layers were deposited through a shadow mask. The layer thickness and deposition rate were monitored in situ during deposition by an oscillating quartz thickness monitor. OLED properties were measured using a Keithley source meter 2400 and a Konica Minolta CS-2000. Luminance ($L$), external EL quantum efficiency ($\eta_{\text{ext}}$), current efficiency ($\eta_c$), and power efficiency ($\eta_p$) were corrected by Lambertian factors of the devices estimated from the angular dependence of the EL intensity.

![Schematic energy-level diagram for OLEDs based on 1–4 as emitters](image)

**Fig. S19** (a) Schematic energy-level diagram for OLEDs based on 1–4 as emitters and (b) molecular structures of the materials used in the devices.
The angular dependence of the EL intensities with the Lambertian distribution of (a) devices A–D and (b) E and F. Lambertian factors were calculated to be 0.835, 0.838, 0.847, 0.837, 0.854, and 0.873 for devices A–F, respectively.

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