Electronic Supplementary Information (ESI)

Axially chiral 1,1'-bicarbazolyls with near-ultraviolet circularly polarized luminescence

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1. General methods

¹H and ¹³C NMR spectra were recorded on an Avance III 400 spectrometer (Bruker). Chemical shifts of ¹H and ¹³C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and CDCl₃ ($\delta = 77.0$) as internal standards, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex III spectrometer (Bruker Daltonics) using dithranol as the matrix. Elemental analysis was carried out using an MT-5 CHN corder (Yanaco).

Enantiomeric resolutions were conducted using by chiral high-performance liquid chromatography (HPLC) monitored at 285 nm performed with a CHIRAL ART Amysolse-SA column (20 mm I.D. \times 250 mm L) (YMC).

Single crystals of **BiCz-1** suitable for the crystallographic analysis were grown from solutions of chloroform/methanol. X-ray crystallographic analysis was performed on a XtaLAB Synergy R, DW system, with a HyPix diffractometer. The crystal was kept at 90 K during data collection. Using Olex2,¹ the structure was solved with the SHELXT² program using Intrinsic Phasing and refined with the SHELXL³ refinement package using Least Squares minimization. The crystallographic data of **BiCz-1** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication materials (CCDC numbers: 2151609). These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data request/cif.

2. Photophysical measurements

UV-vis absorption and photoluminescence (PL) spectra were measured using a V-670Y spectrometer (Jasco) and an FP-8600Y spectrophotometer (Jasco), respectively. The absolute PL quantum yields (Φ_{PL}) were determined using an ILF-835 integrating sphere system (Jasco) under N₂. The transient PL decay measurements were carried out using a C11367 Quantaurus-tau fluorescence lifetime spectrometer (Hamamatsu Photonics) with an LED excitation source ($\lambda_{ex} = 340$ nm, pulse width = 100 ps, repetition rate = 20 Hz) under N₂. The PL lifetimes were extracted from the resulting decay curves by performing exponential fitting and deconvolution with the instrument response function. The photophysical rate constants for radiative decay (k_r) and non-radiative decay (k_{nr}) were calculated according to the equations: $k_r = \Phi_{PL}/\tau$; $k_{nr} = (1-\Phi_{PL})/\tau$, where τ is emission lifetimes for fluorescence.

Circular dichroism (CD) spectra were measured using a J-1500 spectrophotometer (Jasco) at room temperature and were recorded over a wavelength range of 450–280 nm with 1 nm spectral bandwidth. Circularly polarized luminescence (CPL) and DC (= nonpolarized fluorescence) spectra were measured using a Comprehensive Chiroptical Spectrophotometer (CCS-1)⁴ equipped with the Stokes-Mueller matrix analysis system. The excitation wavelength was set to be 310 nm and the emission spectra were recorded over a wavelength range of 500–340 nm with 810–840 V high-tension voltage, 33 mm slit width, and 10 nm spectral bandwidth for the excitation and emission monochromators. The PL dissymmetry factors (g_{lum}) were calculated according to $g_{lum} = \Delta F (= I_L - I_R)/F (= I_L + I_R)$, where I_L and I_R are the intensities of the left- and right-handed CPL emissions.⁵

3. Computational simulations

Density functional theory (DFT) calculations were performed using the GAUSSIAN 16 program package.⁶ Molecular geometries in the ground state (S_0) were optimized using the B3LYP-D3 functional with the 6-31G(d) basis set in the gas phase. The lowest excited singlet and triplet states (S_1 and T_1) were computed using the optimized structures with time-dependent DFT (TD-DFT) at the same level.

4. Synthesis and characterization

All regents 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. The ¹H and ¹³C NMR spectra of (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2** are provided in Fig. S1–S2.

Synthesis of BiCz-H



Scheme S1 Synthesis of BiCz-H.

BiCz-H: To a solution of 3,6-di-*tert*-butylcarbazole (22.4 g, 80.0 mmol) in CH₃CN (1200 mL) was slowly added Cu(ClO₄)₂·6H₂O (0.2 M in CH₃CN, 400 mL, 80.0 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C. After quenching by the addition of K₂CO₃ *aq*. (3.2 M, 100 mL), the product was extracted with CHCl₃. The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: CHCl₃), preparative gel permeation chromatography (eluent: CHCl₃), followed by recrystallization from CHCl₃/methanol to afford **BiCz-H** as a white

solid (yield = 12.5 g, 56%). ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, J = 1.8 Hz, 2H), 8.15 (d, J = 2.0 Hz, 2H), 7.80 (s, 2H), 7.64 (d, J = 2.0 Hz, 2H), 7.46 (dd, J = 8.5, 2.0 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 1.53 (s, 18H), 1.47 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 143.10, 142.62, 138.03, 135.94, 124.31, 123.83, 123.58, 121.45, 116.36, 115.81, 110.33, 34.91, 34.75, 32.16, 32.04 138.29 (One aromatic signal could not be observed probably because of the overlapping). MS (MALDI-TOF): m/z calcd 556.38 [M]⁺; found 556.16.

Synthesis of (rac)-BiCz-1



Scheme S2 Synthesis of (*rac*)-BiCz-1.

(*rac*)-**BiCz-1**: A mixture of **BiCz-H** (1.67 g, 3.0 mmol), *tert*-butyl-4-iodobenzene (5.4 mL, 30.0 mmol), copper (0.46 g, 7.2 mmol), K₂CO₃ (2.90 g, 21.0 mmol), and 18-crown-6 (0.16 g, 0.60 mmol) was stirred at 150 °C for 23 h. After cooling to room temperature, the reaction mixture was added into a large amount of water and then extracted with CHCl₃. The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: CHCl₃/hexane = 1:5, v/v), followed by recrystallization from CHCl₃/CH₃OH to afford (*rac*)-**BiCz-1** as a white solid (yield = 2.31 g, 94%). ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 1.5 Hz, 2H), 7.72 (d, *J* = 1.8 Hz, 2H), 7.49 (d, *J* = 2.0 Hz, 2H), 7.31 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.10-7.04 (m, 4H), 6.46 (m, 4H), 6.19 (s, 2H), 1.54 (s, 23H, overlapping with H₂O), 1.43 (s, 18H), 1.11 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 147.40, 141.89, 139.93, 136.10, 133.57, 125.56, 125.32, 124.29, 123.89, 123.63, 123.36, 122.89, 122.85, 115.91, 114.90, 108.92, 34.61, 34.58, 34.08, 32.26, 32.04, 31.09 (Two aromatic signals could not be observed probably because of the overlapping). MS (MALDI-TOF): *m/z* calcd 820.57 [*M*]⁺; found 820.65. Anal. calcd (%) for C₆₀H₇₂N₂: C 87.75, H 8.84, N 3.41; found: C 87.70, H 8.85, N 3.42.

Synthesis of (rac)-BiCz-2



Scheme S3 Synthesis of (*rac*)-BiCz-2.

(*rac*)-**BiCz-2**: A mixture of **BiCz-H** (1.67 g, 3.0 mmol), 4-iodobenzonitrile (3.44 g, 15.0 mmol), copper (0.46 g, 7.2 mmol), K₂CO₃ (2.90 g, 21.0 mmol), and 18-crown-6 (0.16 g, 0.60 mmol) in dry DMF (36 mL) was stirred at 150 °C for 17 h. After cooling to room temperature, the reaction mixture was added into a large amount of water and then extracted with ethyl acetate. The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 1:2, v/v), followed by recrystallization from CH₂Cl₂/CH₃OH to afford (*rac*)-**BiCz-2** as a white solid (yield = 1.83 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 1.5 Hz, 2H), 7.86 (d, *J* = 2.0 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 2H), 7.38 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.03 (dd, *J* = 8.5, 0.5 Hz, 2H), 6.73-6.68 (m, 8H), 1.54 (s, 18H), 1.47 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 144.47, 144.25, 140.42, 139.05, 135.31, 130.58, 125.25, 124.94, 124.07, 123.68, 123.45, 118.17, 116.33, 115.58, 108.63, 108.56, 34.77, 32.19, 31.92 (One aromatic signal could not be observed probably because of the overlapping). MS (MALDI-TOF): *m/z* calcd 758.43 [*M*]⁺; found 758.60. Anal. calcd (%) for C₅₄H₅₄N₄: C 85.45, H 7.17, N 7.38; found: C 85.21, H 7.19, N 7.32.



Fig. S1 ¹H and ¹³C NMR spectra of (*rac*)-BiCz-1 in CDCl₃.



Fig. S2 ¹H and ¹³C NMR spectra of (*rac*)-BiCz-2 in CDCl₃.



Fig. S3 Chiral HPLC chromatogram for BiCz-H.



Fig. S4 Chiral HPLC chromatograms for (a) **BiCz-1** and (b) **BiCz-2** before optical resolution (left) and after separation of the (R)- and (S)-enantiomers (right). e.e. = enantiomeric excess.



Fig. S5 Chiral HPLC chromatograms for (a) (*S*)-**BiCz-1** and (b) (*S*)-**BiCz-2** after 1 day strage at room temperature (left) and after heating at 100 °C for 1 h (right) in toluene solutions.



Fig. S6 (a) Molecular structure and frontier orbital distributions of (*S*)-**BiCz-1** at an optimized S_0 geometry and (b) theoretical absorption spectrum of (*rac*)-**BiCz-1** simulated with TD-DFT at the B3LYP-D3/6-31G(d) level in gas phase (top) and corresponding experimental absorption spectrum measured in toluene (bottom).



Fig. S7 (a) Molecular structure and frontier orbital distributions of (*S*)-**BiCz-2** at an optimized S_0 geometry and (b) theoretical absorption spectrum of (*rac*)-**BiCz-2** simulated with TD-DFT at the B3LYP-D3/6-31G(d) level in gas phase (top) and corresponding experimental absorption spectrum measured in toluene (bottom).

C 1	$\lambda_{ m PL}$	FWHM	$arPhi_{ ext{PL}}$	τ	$k_{ m r}$	k _{nr}	$\Delta E_{ m ST}$	
Compound	[nm]	[nm]	[%]	[ns]	[10 ⁸ s ⁻¹]	[10 ⁷ s ⁻¹]	[eV]	
(<i>rac</i>)- BiCz-1	377	41	94	4.4	2.2	1.4	0.50	
(<i>rac</i>)- BiCz-2	383	49	44	4.2	1.0	13	0.55	

Table S1 PL data measured in toluene solutions



Fig. S8 Fluorescence (300 K, black line) and phosphorescence (77 K, red line) spectra of (a) (*rac*)-**BiCz-1** and (b) (*rac*)-**BiCz-2** in toluene (10^{-5} M).



Fig. S9 Experimental CD spectra (solid line) in toluene for (a) first and (b) second fractions of HPLC, and theoretical CD spectra (dotted line) of (*R*) and (*S*)-enantiomers of **BiCz-1** (black) and **BiCz-2** (blue) simulated with TD-DFT at the B3LYP-D3/6-31G(d) level.



Fig. S10 (a) CD spectra and (b) corresponding g_{abs} vs. wavelength curves of enantiopure (*R/S*)-**BiCz-1** (upper) and (*R/S*)-**BiCz-2** (lower) in toluene solutions.



Fig. S11 (a) UV–vis absorption and (b) PL spectra of (*R*)- and (*S*)-enantiomers of **BiCz-1** (black) and **BiCz-2** (blue).

E	С	λ_{ex}	$\lambda_{ m PL}$	FWHM	$g_{ ext{lum}}$ at $\lambda_{ ext{PL}}$	$g_{ m lum,ave}$
Enantiomer	[10 ⁻⁴ M]	[nm]	[nm]	[nm]	[10-4]	[10-4]
(<i>R</i>)- BiCz-1	1.9	310	374	37	3.6	2.2
(S)-BiCz-1	2.8	310	374	37	-4.7	-2.8
(<i>R</i>)- BiCz-2	4.4	310	376	42	5.8	3.8
(S)- BiCz-2	4.0	310	379	42	-6.4	-4.0

Table S2 CPL data of (R)- and (S)-enantiomers in toluene

Average PL dissymmetry factors ($g_{lum,ave}$) were calculated from ranges of each emission peaks ± 20 nm.





(S)-BiCz-1



(S)-BiCz-2

Fig. S12 Molecular structures and the electric and magnetic transition dipole moments (μ and m) of (S)-BiCz-1 and (S)-BiCz-2 at the S₁ geometries calculated at the B3LYP-D3/6-31G(d) level.

	5	5			
Enantiomer	$ \mu_{\rm cal} $	$ m_{\rm cal} $	$ \cos\theta $	$ g_{ m cal} $	
	$[10^{-20} \text{ esu cm}]$	$[10^{-20} \text{ erg } \text{G}^{-1}]$			
(S)-BiCz-1	280	1.3	0.09	1.7×10^{-3}	
(S)- BiCz-2	91	0.27	0.23	2.7×10 ⁻³	

Table S3 Theoretical PL dissymmetry factors of (S)-BiCz-1 and (S)-BiCz-2

 μ_{cal} : calculated electric transition dipole moment; m_{cal} : calculated magnetic transition dipole moment; g_{cal} : theoretical PL dissymmetry factor.

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