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

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The facile synthesis and chiroptical properties of a new family of circularly polarized luminescence (CPL) materials, axially chiral 1,1'-bicarbazolyls (BiCz), is reported. The BiCz derivatives emitted intense near-ultraviolet photoluminescence, with a peak at ~380 nm. The BiCz enantiomers showed mirror-image circular dichroism and CPL, with g_{lum} values on the order of 10^{-4} in solution.

Axially chiral biaryls, typified by 1,1’-binaphthyl derivatives, are indispensable stereogenic motifs for chiral ligands and chiral organocatalysts in asymmetric synthesis.[1,2] Apart from their use in organic synthesis, the development of axially chiral biaryls as chiroptical functional π-materials[3] with circularly polarized luminescence (CPL) properties has gained increasing interest.[4] The interest in CPL materials stems from their prospective applications in 3D displays,[5] optical quantum information[6] and security systems,[7] biological probes/sensors,[8] and the control of plant growth. The use of axially chiral 1,1’-binaphthyl has enabled the development of a variety of CPL-active materials, including organic fluorophores,[4a,i,j,9,10] thermally activated delayed fluorescence (TADF) emitters,[4b,c,5b,11] and metal complex phosphors.[12] However, the structural variety and functional extensibility are relatively low because they rely on the conventional 1,1’-binaphthyl scaffold.

Carbazole is among the most widely used π-conjugated building unit, finding prominent utility in optoelectronic device applications including organic light-emitting diodes (OLEDs).[13] This widespread use prompted us to design a novel, functional axially chiral motif featuring carbazole. However, the reports on carbazole-based CPL materials are still scarse.[14] It is well known that carbazole are readily functionalized by electrophilic aromatic substitution at the 3,6-positions (*para* positions from the nitrogen atom) with high electron densities. Therefore, further functionalization of the carbazole at the 1,8-positions (*ortho* positions from the nitrogen atom) can proceed by protecting the most reactive 3,6-positions. The 3,6-di-substituted 1,1’-bicarbazolyl (**BiCz-H**) framework can be constructed by Ni(0)-mediated dehalogenative coupling (Yamamoto coupling) or oxidative coupling.[15] To produce left- and right-handed CPL, the (*R*)- and (*S*)-enantiomeric forms of the chiral substance must be prepared. However, isolating the non-racemic (enantiomeric) forms of **BiCz-H** is impossible because the aryl–aryl bond is not sterically congested (Fig. 1a). Therefore, further *N*-arylation of **BiCz-H** is exploited herein to induce a large rotational barrier to yield a resolvable 1,1’-bicarbazolyl-based chiral π-system. The simplicity and versatility of this post-*N*-functionalization enable further exploration of the potential of 1,1’-bicarbazolyl derivatives as CPL materials. Herein, we report the facile synthesis of axially chiral 1,1’-bicarbazolyls, **BiCz-1** and **BiCz-2** (Fig. 1b), and their fundamental photophysical and chiroptical properties.

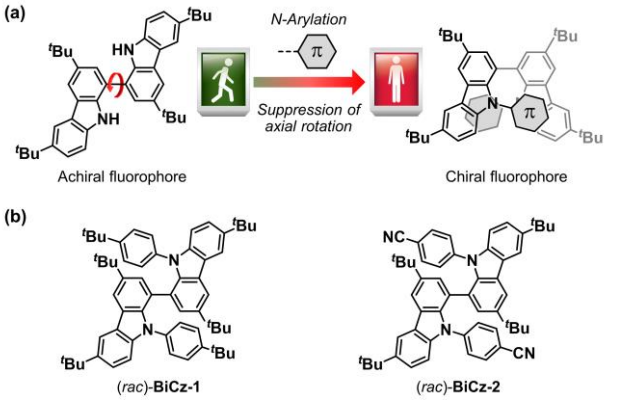

Fig. 1 (a) Design of novel axially chiral 1,1’-bicarbazolyls and (b) chemical structures of **BiCz-1** and **BiCz-2**.

Scheme 1 outlines the facile two-step synthesis of the racemic 1,1’-bicarbazolyls, (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2**, from commercially available 3,6-di(*tert*-butyl)carbazole. $Cu(ClO_4)_2$ was used for the direct oxidative coupling of 3,6-di(*tert*-butyl)carbazole under the optimized conditions to furnish

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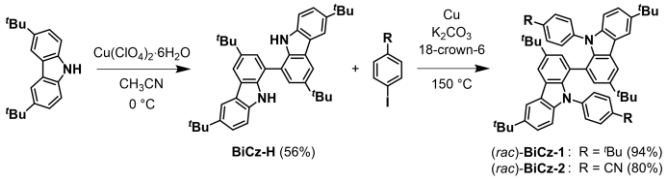
dimeric **BiCz-H** in 56% yield. Subsequently, **BiCz-H** was subjected to Ullmann coupling with 1-(*tert*-butyl)-4-iodobenzene and 4-iodobenzonitrile to afford (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2** in 94% and 80% yields, respectively. The chemical structures of these products were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis (ESI†). Successive optical resolutions were achieved using preparative HPLC on a chiral stationary phase, affording sufficient of both enantiomers of **BiCz-1** and **BiCz-2** in >99% enantiomeric excess (e.e.). The absolute configurations for the first fractions of **BiCz-1** and **BiCz-2** in the chiral HPLC analyses could be determined as (*S*)-**BiCz-1** and (*S*)-**BiCz-2**, respectively, by comparison of the experimental circular dichroism (CD) spectra and computational simulation results (ESI†). The *N*-aryl groups effectively suppressed racemization of both enantiomers, allowing them to retain stable axial chirality, unlike unsubstituted **BiCz-H**. Both resolved (*S*)-**BiCz-1** and (*S*)-**BiCz-2** were found to retain >99% e.e. in toluene solution even when kept for 1 day at room temperature. However, upon heating the solutions at 100 °C for 1 h, the e.e. decreased to 95% and 90%, respectively (ESI†).



Scheme 1 Synthesis of axially chiral 1,1'-bicarbazolyl derivatives.

X-ray crystallographic analysis revealed that (*rac*)-**BiCz-1** crystallized in the orthorhombic *Pbca* space group (Fig. 2 and ESI†). In a single crystal of (*rac*)-**BiCz-1**, there are eight molecules per unit cell, comprising four of each (*R*)- and (*S*)-enantiomer with mirror symmetry. The dihedral angles of the central 1,1'-bicarbazolyl units are all approximately ±60°, suggestive of large steric hindrance around the chiral axis.

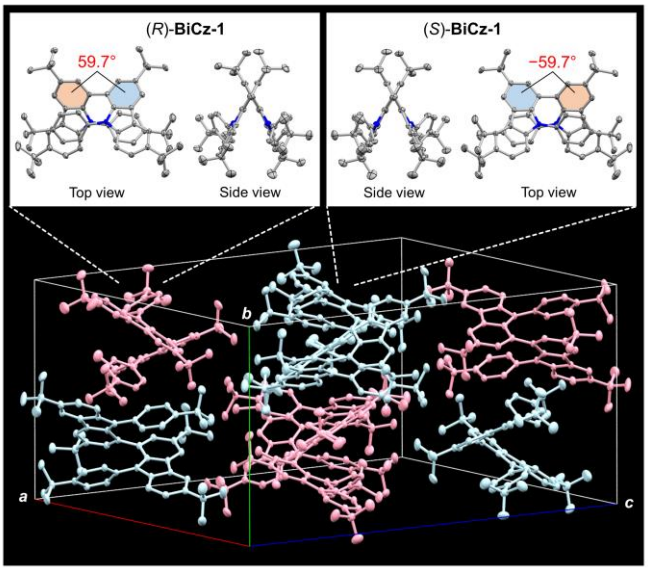


Fig. 2 X-ray crystal structure of (*rac*)-**BiCz-1** (CCDC No. 2151609): (top) ORTEP drawings of (*R*)-**BiCz-1** (left) and (*S*)-**BiCz-1** (right) enantiomers with thermal ellipsoids at the 50% probability level; (bottom) molecular packing diagram containing equimolar (*R*)- and (*S*)-enantiomers (pink and light-blue molecules, respectively). Hydrogen atoms and solvent molecules ($CHCl_3$) are omitted for clarity.

To gain insight into the molecular geometries and electronic transition characteristics, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed for **BiCz-1** and **BiCz-2** at the B3LYP-D3/6-31G(d) level (Fig. 3).[16] In **BiCz-1** and **BiCz-2**, the 1,1'-bicarbazolyl units adopted a highly twisted geometry around the chiral axis in the ground state (S_0), with dihedral angles were 58.8° and 54.9°, respectively. This result is consistent with the aforementioned crystallographic data. For 4-*tert*-butylphenyl-substituted **BiCz-1**, the lowest singlet (S_1) excitation was dominated by the HOMO → LUMO transition with π–π* characteristics. Contrastingly, in 4-cyanophenyl-substituted **BiCz-2**, the S_1 excitation was characterized by a forbidden HOMO → LUMO transition with intramolecular charge transfer (ICT) characteristics. In this transition, the HOMO was distributed over the entire molecule, whereas the LUMO was mainly localized on the electron-accepting 4-cyanophenyl groups. The intensive electronic excitations corresponded to the allowed HOMO−1 → LUMO ICT transition (S_4) and HOMO → LUMO+2 π–π* transition (S_5), with relatively large oscillator strengths (*f* = 0.1844 and 0.0754, respectively).

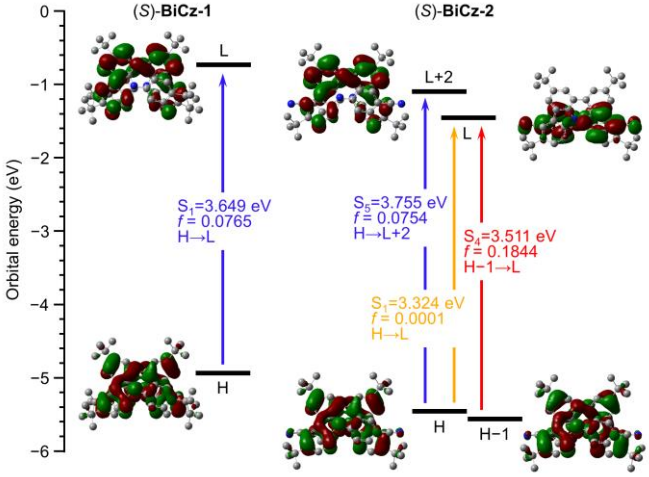


Fig. 3 Electronic transition and associated Kohn–Sham orbitals for (*S*)-**BiCz-1** (left) and (*S*)-**BiCz-2** (right) in optimized S_0 geometries, calculated at the B3LYP-D3/6-31G(d) level in the gas phase. H = HOMO; L = LUMO.

Fig. 4 shows the photophysical spectroscopic properties of (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2** in toluene, including the UV–vis absorption and photoluminescence (PL) spectra and transient PL curves. The lowest-energy absorption band of (*rac*)-**BiCz-1** was observed at 355 nm, and was assigned to the π–π* transition. (*rac*)-**BiCz-1** also emitted intense near-ultraviolet (NUV) photoluminescence (PL) with a peak (λ_{PL}) at 377 nm; the absolute PL quantum yield (Φ_{PL}) was as high as 94%. Notably, the spectral full width at half maximum (FWHM) of (*rac*)-**BiCz-1** was as small as 41 nm, which reflects its rigid molecular structure. As predicted by the TD-DFT calculations (Fig. 3), a very weak ICT absorption centered at 450 nm was observed for (*rac*)-**BiCz-2**. However, the PL of (*rac*)-**BiCz-2** predominantly occurred in the NUV region (λ_{PL} = 383 nm), similar to (*rac*)-**BiCz-1** (Fig. 4b,c). The Φ_{PL} of (*rac*)-**BiCz-2** (44%) was less than half that of (*rac*)-**BiCz-1**, most likely because of deactivation through non-radiative internal conversion and/or intersystem crossing. The transient PL characteristics of both compounds had similar monoexponential emission decays with lifetimes (τ) of 4.2–4.4

ns at 300 K (Fig. 4d), indicative of typical fluorescence properties. Based on these photophysical data, the fluorescence radiative decay rate ($k_r = \Phi_{PL}/\tau$) and the non-radiative decay rate ($k_{nr} = (1 - \Phi_{PL})/\tau$) can be assessed. Both (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2** had comparably high k_r values of 2.1×10^8 and 1.0×10^8 s^{-1}, respectively; however, the k_{nr} of (*rac*)-**BiCz-2** (1.3×10^8 s^{-1}) was one order of magnitude larger than that of (*rac*)-**BiCz-1** (1.4×10^7 s^{-1}). Moreover, no distinct TADF properties were observed for either compound because of their considerably large singlet–triplet energy gap (ΔE_{ST} >0.5 eV; ESI†) with respect to the ambient thermal energy ($k_BT \approx 25.9$ meV at 300 K).

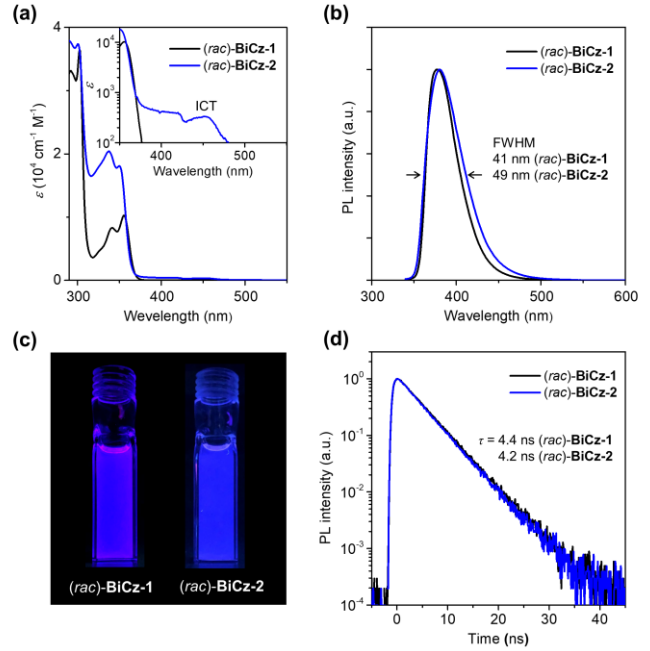


Fig. 4 (a) UV–vis absorption and (b) steady-state PL spectra of (*rac*)-**BiCz-1** and (*rac*)-**BiCz-2** in deoxygenated toluene solutions (10^{-5} M). The inset of (a) shows a magnified view of the lower-energy ICT absorption. (c) Photograph showing NUV emissions from the solutions under UV illumination at 365 nm. (d) Transient PL decay curves measured for the solutions at 300 K.

Circular dichroism (CD) and CPL spectra were acquired to examine the chiroptical properties of the (*R*/*S*)-**BiCz-1** and (*R*/*S*)-**BiCz-2** enantiomer pairs in toluene for the ground and excited states. As shown in Fig. 5a, the CD spectra of the enantiomers exhibited clear mirror-image relationships with strong Cotton effects at 355 nm and absorption dissymmetry factors ($|g_{abs}|$) of 2×10^{-3} (ESI†), which correspond to the π–π* absorption on the chiral 1,1′-bicarbazolyl skeleton. However, (*R*/*S*)-**BiCz-2** had no significant Cotton effect in the ICT absorption region. The CPL spectra of the (*R*/*S*)-**BiCz-1** and (*R*/*S*)-**BiCz-2** solutions showed mirror-image CPL signals (Fig. 5a) with PL dissymmetry factors ($|g_{lum}|$) of 4×10^{-4} and 6×10^{-4}, respectively, at the λ_{PL} positions (Fig. 5b). Although the obtained $|g_{lum}|$ values are within the normal range for reported CPL materials made from axially chiral biaryls, the luminescence efficiencies can be greatly improved by using the 1,1′-bicarbazolyl π-core instead.

In theory, g_{lum} is determined as follows:[17]

$$g_{\mathrm{lum}} = \frac{2(I_{\mathrm{L}} - I_{\mathrm{R}})}{(I_{\mathrm{L}} + I_{\mathrm{R}})} = \frac{4|\mu||m|\cos\theta}{|\mu|^2 + |m|^2} \qquad (1)$$

where I_L and I_R are the intensities of the left- and right-handed CPL emissions, μ and m are the electric and magnetic transition dipole moments, respectively, and θ represents the angle between the μ and m vectors. Complete left- and right-handed CPL lights lead to the maximum g_{lum} values of +2 and −2, respectively. Using TD-DFT calculations, $|\mu|$, $|m|$, and θ for **BiCz-1** and **BiCz-2** were simulated,[16] considering their dominant π–π* and ICT transitions, respectively (ESI†). Consequently, **BiCz-2** exhibited a slightly larger theoretical dissymmetry factor ($|g_{cal}| = 2.7 \times 10^{-3}$) than **BiCz-1** ($|g_{cal}| = 1.7 \times 10^{-3}$), which is reasonably consistent with the trend of the experimental $|g_{lum}|$ values. In the optimized **BiCz-1** and **BiCz-2** molecules, the μ and m vectors had nearly perpendicular orientations (ESI†), resulting in a small $|\cos\theta|$ (0.09 and 0.23, respectively) and small $|g_{lum}|$ on the order of 10^{-4}.

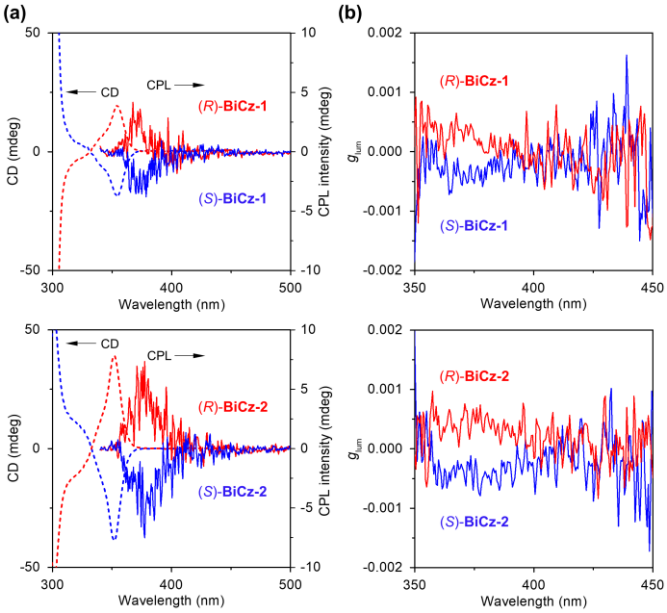


Fig. 5 (a) CD (dashed lines) and CPL (solid lines) spectra and (b) corresponding g_{lum} vs. wavelength curves of enantiopure (*R*/*S*)-**BiCz-1** (upper) and (*R*/*S*)-**BiCz-2** (lower) in toluene solutions (10^{-4} M).

In summary, the first axially chiral 1,1′-bicarbazolyl derivatives, (*R*/*S*)-**BiCz-1** and (*R*/*S*)-**BiCz-2**, were successfully developed. These materials can be readily synthesized in two steps with high yields. These pairs of enantiomers can emit highly efficient PL in the NUV region, with distinct CPL activity in solution. This study is expected to stimulate the exploration of functional π-materials based on axially chiral 1,1′-bicarbazolyls for chiroptical applications. Further study on material design to enhance the dissymmetry factor is currently underway.

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Conflicts of interest

There are no conflicts to declare.

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