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Author(s)	Takishima, Ryo; Nishii, Yuji; Miura, Masahiro
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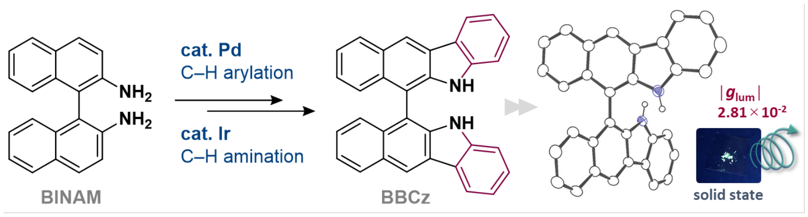
Note	

Synthesis and Optical Properties of Axially Chiral Bibenzo[*b*]carbazole (BBCz) Derivatives

Ryo Takishima,[†] Yuji Nishii,*[,†] and Masahiro Miura*[,†]

[†] Department of Applied Chemistry, Graduate School of Engineering, Suita, Osaka 565-0871, Japan

Supporting Information Placeholder

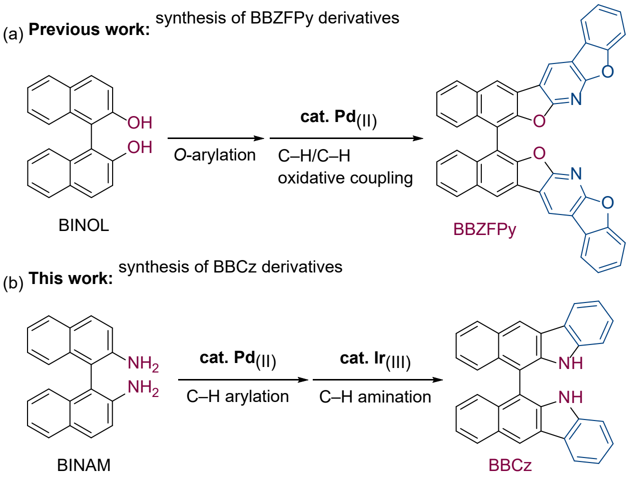


ABSTRACT: Pure organic materials with the circularly polarized luminescence (CPL) property have attracted significant research interests over the past few decades. In this study, a series of axially chiral bibenzo[*b*]carbazole (BBCz) derivatives were synthesized adopting palladium- and iridium-catalyzed direct C–H functionalization reactions as the key steps. These compounds exhibited CPL characteristics with considerably large dissymmetry factors up to 2.81×10^{-2} in the solid state, indicating the formation of well-ordered aggregates. The packing structure of BBCz itself was evaluated by X-ray analysis to disclose a strong N–H···π hydrogen bonding interaction.

Optically active poly(hetero)aromatic compounds have been a key motif in a wide range of functional molecules because of their tremendous utility as electrochemical and photophysical materials. A major advantage of pure organic materials is fine-tuning of the properties by chemical modification. Recently, chiroptical functional materials bearing circularly polarized luminescence (CPL)[1] characteristics have attracted widespread attention for their potential applications in three-dimensional displays,[2] information storage systems,[3] biological probes,[4] photocatalysis,[5] etc. A key parameter in developing high-performance CPL materials is dissymmetry factor g_{lum}, ranging between -2 and +2.[6] However, the g_{lum} value of pure organic molecules is usually small within the range of 10^{-5}~10^{-3}, and thus effective synthetic strategies are in high demand to explore new chiral scaffolds.

Among a series of chiral scaffolds for CPL emitting molecules, axially chiral binaphthyl compounds have been extensively studied because of the availability of both enantiomers in low cost and the ease of site-selective functionalization. The most common approach is tethering achiral π-conjugated chromophores on the periphery of biaryls.[7] On the other hand, axially chiral CPL active molecules with π-extended poly(hetero)aromatic skeletons have been scarce probably because of the synthetic difficulty to get them as pure enantiomers.[8] Upon this concept, we previously achieved the synthesis of chiral bisbenzofuro[2,3-*b*:3′,2′-*e*]pyridine (BBZFPy) derivatives utilizing the palladium-catalyzed C–H/C–H oxidative coupling reaction,[9] embedding the hydroxy groups of 1,1’-bi-2-naphtol (BINOL) into the polyaromatic scaffolds (Scheme 1a).[10] These compounds exhibited CPL characteristics, and unique aggregation-induced improvement of the g_{lum} value up to 6.68×10^{-3} was observed.

Scheme 1. Synthesis of Binaphthyl-Based Polyaromatic Compounds via the Direct C–H Functionalization



Meanwhile, a limited number of CPL active compounds have been developed based on 1,1’-bi-2-naphthylamine (BINAM),[11] an amine analog of BINOL. We thus envisioned that the assembly of nitrogen-based π-conjugated chromophores embedding the amine groups into the polyaromatic system would produce new chiroptical materials. Actually, indole and carbazole derivatives have been known as potent blue-emitting organic fluorophores. Herein, we report the synthesis of bibenzo[*b*]carbazole (BBCz) derivatives as a new-class of axially chiral luminescence materials (Scheme 1b). These compounds exhibited CPL characteristics with considerably large dissymmetry factors in

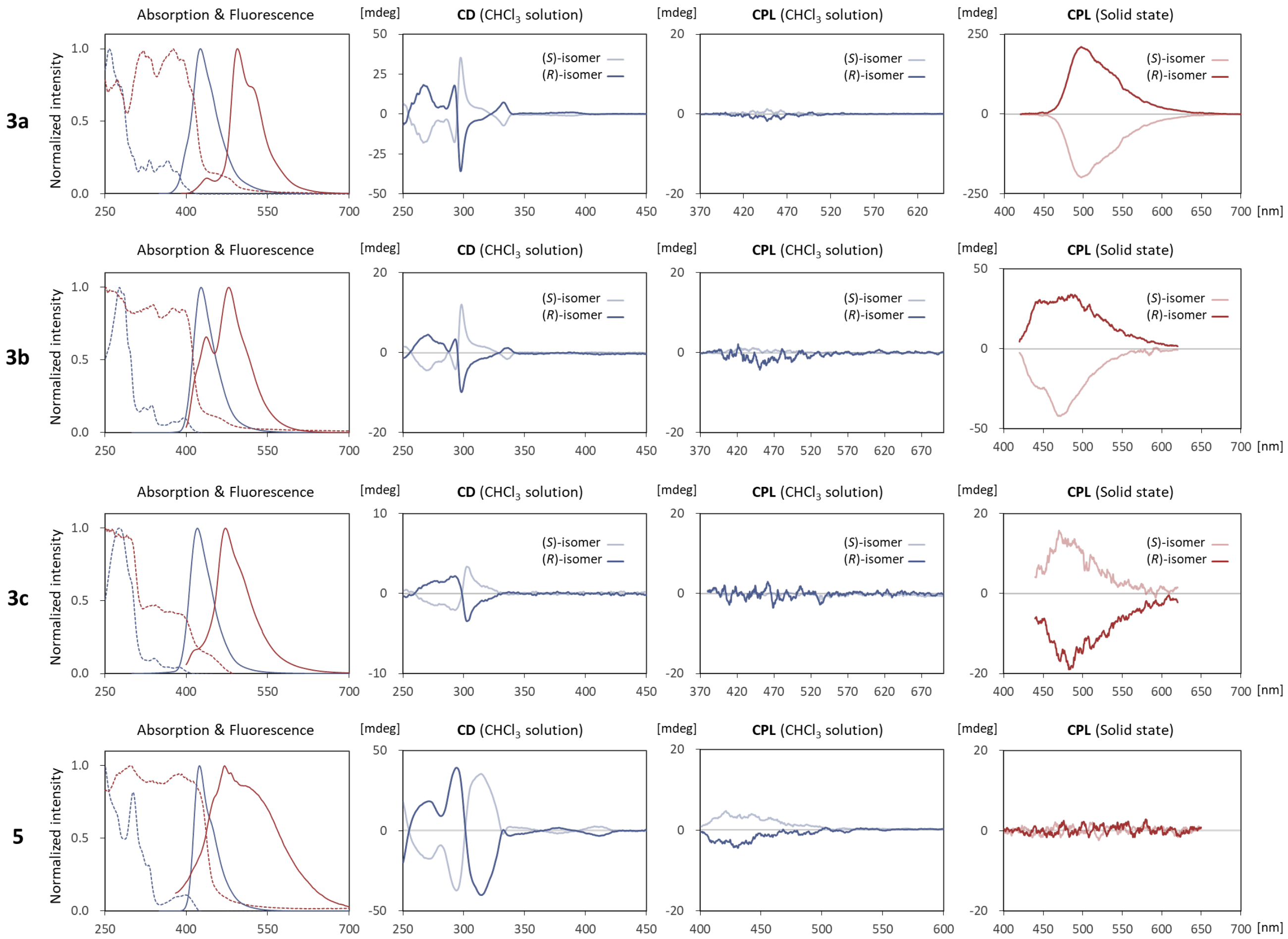
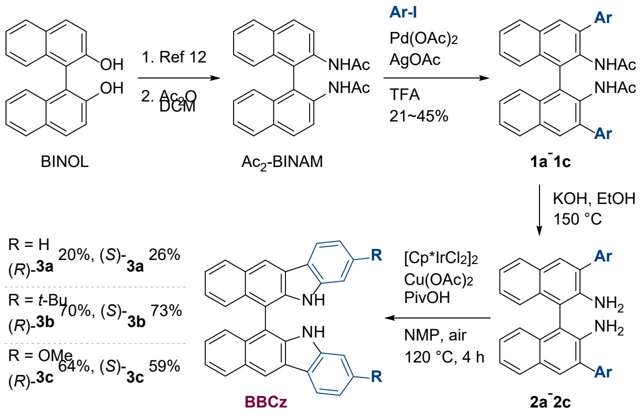


Figure 1. Absorption (dotted line) and fluorescence (solid line) spectra of **3a**, **3b**, **3c**, and **5** were measured as $CHCl_3$ solutions (1.0×10^{-5} M, blue) and in solid states (red). CD and CPL spectra were measured as $CHCl_3$ solutions (1.0×10^{-5} M) or in solid states.

the solid state. The molecular structure and packing system were evaluated by X-ray crystallographic analyses.

The target compounds were synthesized from the commercially available BINOL in five steps (Scheme 2).

Scheme 2. Synthesis of BBCz Derivatives **3**



According to the literature procedure,[12] BINOL was converted to the corresponding diamine (BINAM). After acetylation, the palladium-catalyzed direct C–H arylation reported by Stahl[13,14] was adopted to install aryl groups at C3 and C3' positions to give **1a**–**1c**. The free diamines **2a**–**2c** were then recovered by basic treatment. To our delight, the cyclized BBCz derivatives **3a**–**3c** were obtained in 20~73% yields as optically pure compounds by utilizing the iridium-catalyzed intramolecular amination protocol,[15] which we previously developed.[16] The lower yield of **3a** is probably due to its low solubility. On the other hand, palladium-catalyzed cyclization of **1a** was not successful,[17] giving **3a** in only a negligible amount. The structures of **3** were unambiguously determined by X-ray analyses (CCDC 2052728, 2052729, and 2052730).

Additionally, a pyridine analogue of **3a** was prepared (Scheme 3). BINAM was treated with 2,3-dibromopyridine in the presence of a $Pd(OAc)_2/PPh_3$ catalyst to afford the precursor **4** in high yields. The intramolecular direct coupling was then effected to produce the corresponding bibenzo[*f*]pyrido[2,3-*b*]indoles (BBPI) as a pair of pure enantiomers.[18]

Next, we evaluated the optical and chiroptical properties of the synthesized poly-aromatic molecules. The results are summarized in Figure 1 and Table 1.[19] Both BBCz (**3a**–**3c**) and

BBPI (**5**) are significantly emissive, exhibiting blue fluorescence with moderate to high quantum yields (0.37~0.68) upon excitation. The circular dichroism (CD) spectra showed apparent Cotton signals which are characteristic to axially chiral compounds. The pair of enantiomers apparently draws a mirror image of each other with anisotropy factors g_{abs} of in 10^{-4} to 10^{-3} order.

Scheme 3. Synthesis of BBPI Derivatives **5**

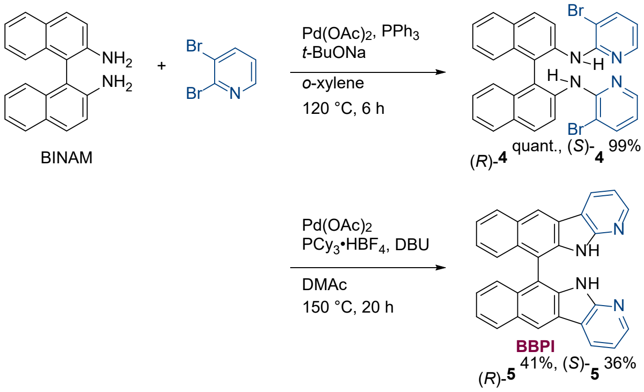


Table 1. Summary of Optical Properties

	Φ (soln.)^a	g_{abs} (soln.)^a	g_{lum} (soln.)^a	Φ (solid)	g_{lum} (solid)
3a	0.38	1.18×10^{-4}	--	0.17	2.81×10^{-2}
3b	0.68	4.42×10^{-4}	--	0.14	6.30×10^{-3}
3c	0.37	1.14×10^{-4}	--	0.04	1.73×10^{-3}
5	0.41	3.35×10^{-3}	3.90×10^{-4}	0.05	--

^{a} Measured as $CHCl_3$ solution (1.0×10^{-5} M).

The BBCz derivatives **3** did not produce clear mirror images in their circularly polarized luminescence (CPL) spectra as $CHCl_3$ solutions. In sharp contrast, these compounds are obviously CPL active in the solid state, and the substituents at C3 and C3' positions considerably affect the luminescence property. The benchmark BBCz **3a** (R = H) showed a remarkably large g_{lum} value of 2.81×10^{-2} even though it is rather a simple axially chiral molecule. A relatively smaller g_{lum} value of 6.30 $\times$ 10^{-3} was given to **3b** (R = *t*-Bu). For these two compounds, the (*S*)-isomers displayed left-handed CPL characteristics for their fluorescence emission bands, whereas the (*R*)-isomers emitted right-handed CPL. Intriguingly, the installation of OMe groups to the carbazole core (**3c**) resulted in the inversion of CPL signals. This is possibly because of the change in their aggregate structures (see below).[20] We also investigated the CPL activity of BBPI **5**. This compound displayed a mirror image more clearly than those of **3** as the $CHCl_3$ solution; however, the spectrum in the solid state was indistinct.

The fact that BBCz derivatives **3** possess substantial dissymmetry factors in the solid state indicates the carbazole ring is an effective motif to consolidate the formation of well-ordered aggregates.[21] Accordingly, we evaluated the interaction within their packing structures by X-ray crystallography (Figure 2). The crystal structure of **3a** was underpinned by a characteristic N–H···π hydrogen bond (ca. 2.66 Å) as well as two C–H···π hydrogen bonds (Figure 2, top). Such a strong N–H···π interaction has been frequently found in the crystal structure of carbazole derivatives,[22] and it is notable that the stabilization effect of N–H···π interactions is generally higher than that of C–H···π interactions.[23] On the other hand, no N–H···π hydrogen bonding was found between the neighboring molecules of **3b** and **3c**, respectively. The *tert*-butyl BBCz **3b** formed 1:1 co-crystals with chloroform,[24] and no obvious intermolecular C–H···π interaction was observed between aromatic moieties (Figure 2, middle). The methoxy BBCz **3c** exhibited a strong N–H···O interaction (2.48 Å) and two C–H···π hydrogen bonds (Figure 2, bottom). Because the unit cell of **3c** was occupied with two independent molecules, two torsion angles of each structure (68° and 62°) are shown. As exemplified herein, different driving forces to consolidate each packing system may greatly affect their chiroptical properties. Therefore, the developed synthetic method, which can systematically and efficiently construct various axially chiral carbazole derivatives, would be highly valuable to explore new organic CPL materials. We also attempted to evaluate the crystal structure of **5** but not successful after numerous trials.

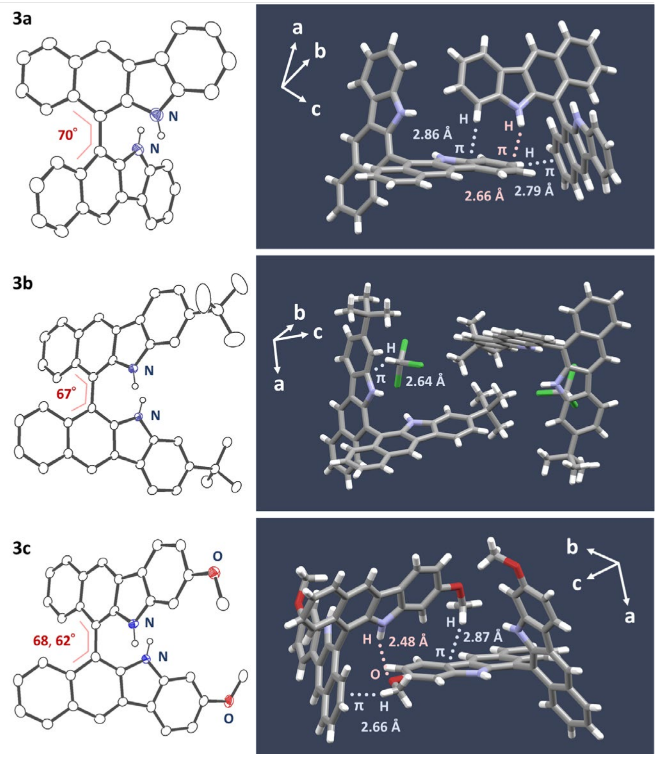


Figure 2. ORTEP drawings with each binaphthyl torsion angle (left) and short contact in molecular packing models (right) of BBCz derivatives **3a** (top), **3b** (middle), and **3c** (bottom).

In conclusion, we synthesized new axially chiral BBCz derivatives adopting palladium-catalyzed direct C–H arylation and iridium-catalyzed direct C–H amination reactions. These compounds exhibited CPL characteristic with considerably large dissymmetry factors up to 2.81×10^{-2} in the solid state. The molecular structure and packing system were evaluated by X-ray crystallographic analyses to find a strong N–H···π hydrogen bonding interaction within **3a**. Further study on the synthesis and CPL characteristics of binaphthyl-fused polyaromatic compounds is currently underway in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

- Experimental procedures, additional spectroscopic data, product identification data, and copy of NMR spectra (PDF)
- Crystallographic data for **3a** (CIF)
- Crystallographic data for **3b** (CIF)
- Crystallographic data for **3c** (CIF)

AUTHOR INFORMATION

Corresponding Author

* y_nishii@chem.eng.osaka-u.ac.jp
* miura@chem.eng.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

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(19) See also Table S1 in the Supporting Information.

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