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Azahelicene-Fused BODIPY Analogs Showing Circularly Polarized Luminescence

Chihiro Maeda,* Keiji Nagahata, Takuma Shirakawa, and Tadashi Ema*[a]

Abstract: Helical carbazole-based BODIPY analogs were readily synthesized via aza[7]helicenes. The structures of azahelicene-incorporated BF_2 dyes were elucidated by X-ray diffraction analysis. DFT calculations revealed that the π-conjugated system expanded from the helicene moiety to the BODIPY framework. The azahelicene-fused boron complexes showed the Cotton effects and the circularly polarized luminescence (CPL) in the visible region. Furthermore, an axially chiral binaphthyl group was attached to the helically chiral dyes, which enhanced the chiroptical properties.

Helicenes are interesting and challenging molecules, and chiroptical properties of helicenes have been actively studied.[1–4] Circularly polarized luminescence (CPL) dyes attract considerable attentions since they have potential applications to chiroptical devices,[3–8] and various helicenes showing CPL have been reported.[3,4] However, most helicenes reported so far showed CPL in a blue region partly because functionalization of helicenes to tune the CPL wavelength is difficult. Some nitrogen-containing helicenes show CPL in a visible light region via coordination, protonation, or donor–acceptor interactions.[3d–f,4f–g]

BODIPY derivatives and congeners have been extensively studied because of the excellent fluorescent properties.[9] Although BODIPY itself is an achiral dye, CD and CPL can be induced by the incorporation of a chiral unit. Indeed, chiral BODIPYs have been recognized as promising CPL materials.[8] We have investigated the synthesis and fluorescence properties of carbazole-based BODIPY analogs,[10] including chiral ones showing CPL (Figure 1).[10e,f] In this study, we used azahelicenes[2,3] to design novel chiral carbazole-based boron complexes as color-tunable CPL dyes. In particular, we aimed for NIR-responsive CPL dyes since such red-shifted CPL dyes have scarcely been reported.[7g] We considered that aza[7]helicenes such as **7** and **10** are good candidates for chiral carbazole-based dyes (Scheme 1). **7** was prepared via the reported method,[2g] while we developed π-extended aza[7]helicene **10** for the first time. These aza[7]helicenes were further converted into the corresponding chiral carbazole-based BODIPY analogs **1**–**6**. These azahelicene-incorporated boron complexes showed red-shifted emission and CPL.

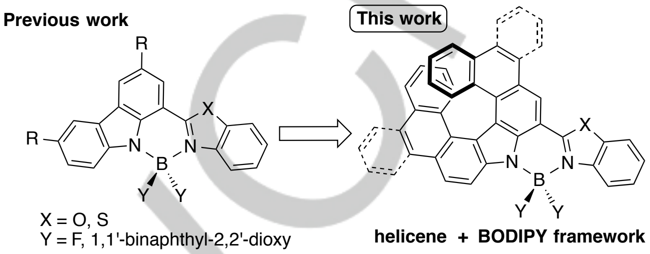
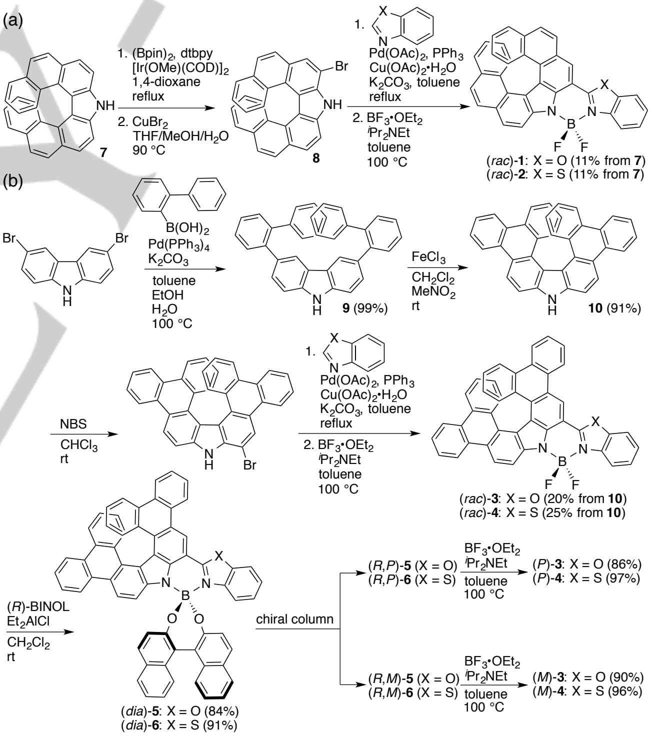


Figure 1. Molecular designs for the chiral carbazole-based boron complexes.



Scheme 1. Synthesis of helical dyes (a) **1**–**2** and (b) **3**–**6**.

First, helical carbazole-based BF_2 dyes **1** and **2** were synthesized as follows (Scheme 1a). The Ir-catalyzed borylation of aza[7]helicene **7** and the subsequent bromination with $CuBr_2$ gave **8**. Direct arylation of **8** with benzoxazole and benzothiazole, followed by the BF_2 complexation afforded (*rac*)-**1** and (*rac*)-**2**, respectively. Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of ethanol into a dichloromethane solution of **2**. X-ray crystal structure of **2** unambiguously elucidated the structure of the azahelicene-incorporated BF_2 dye (Figure 2a).[11a] In the crystal packing, the

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enantiomers (*P*)-**2** and (*M*)-**2** stack alternately to form a 1-D column (Figure S1 in SI). Optical resolution of both racemates using Chiralpak IA gave two fractions which showed mirror-image CD spectra (Figure 3 and S2 in SI). The absolute configurations were determined by TD-DFT calculations of (*P*)-**1** and (*P*)-**2**, and the calculated rotatory strengths were in good agreement with the CD spectra of the first fractions in both cases.

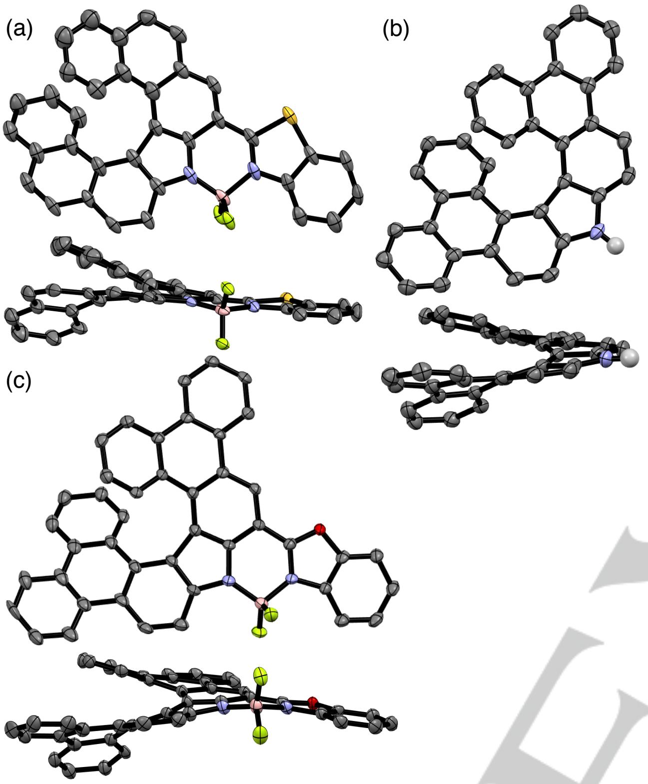

Figure 2. X-ray crystal structures of (a) **2**, (b) **10**, and (c) **3**. Hydrogen atoms except for NH proton and solvent molecules are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

We then synthesized another type of helical carbazole-based BF_2 dyes **3** and **4** with triphenylene units (Scheme 1b). The Suzuki–Miyaura coupling of 3,6-dibromocarbazole with 2-biphenylboronic acid gave 3,6-bis[(1,1'-biphenyl)-2-yl]carbazole (**9**). Oxidative fusion reaction with $FeCl_3$ afforded π-extended aza[7]helicene **10** completely regioselectively. This regiospecific reaction at 4- and 5-positions is surprising because **10** is the most strained regioisomer of the three possible regioisomers.[12] The structure of helical π-extended carbazole **10** was confirmed by X-ray diffraction analysis (Figure 2b).[11b] Treatment of **10** with NBS gave monobrominated compound **11**. Direct arylation of **11** with benzoxazole and benzothiazole, followed by the BF_2 complexation afforded (*rac*)-**3** and (*rac*)-**4**, respectively. The structure of **3** was determined by X-ray diffraction analysis to show the π-extended helical carbazole-based BF_2 dye (Figure 2c).[11c] The aza[7]helicene moiety of **3** is quite similar to the structure of **10**. We then attempted the optical resolution of **3** and **4** using a chiral HPLC column, which resulted in failure because of the low solubility. Therefore, we converted **3** and **4** into (*dia*)-**5** and (*dia*)-**6**, respectively, with binaphthyl units via the Et_2AlCl-mediated reaction. The diastereomeric mixtures were successfully separated by chiral HPLC (SI). The optically pure **5** and **6** were then converted back into enantiomerically pure **3** and **4**, respectively, under the standard BF_2 complexation conditions. The absolute configurations were determined by TD-DFT calculations of (*P*)-**3**–**6** (Figure 3b and 3c).

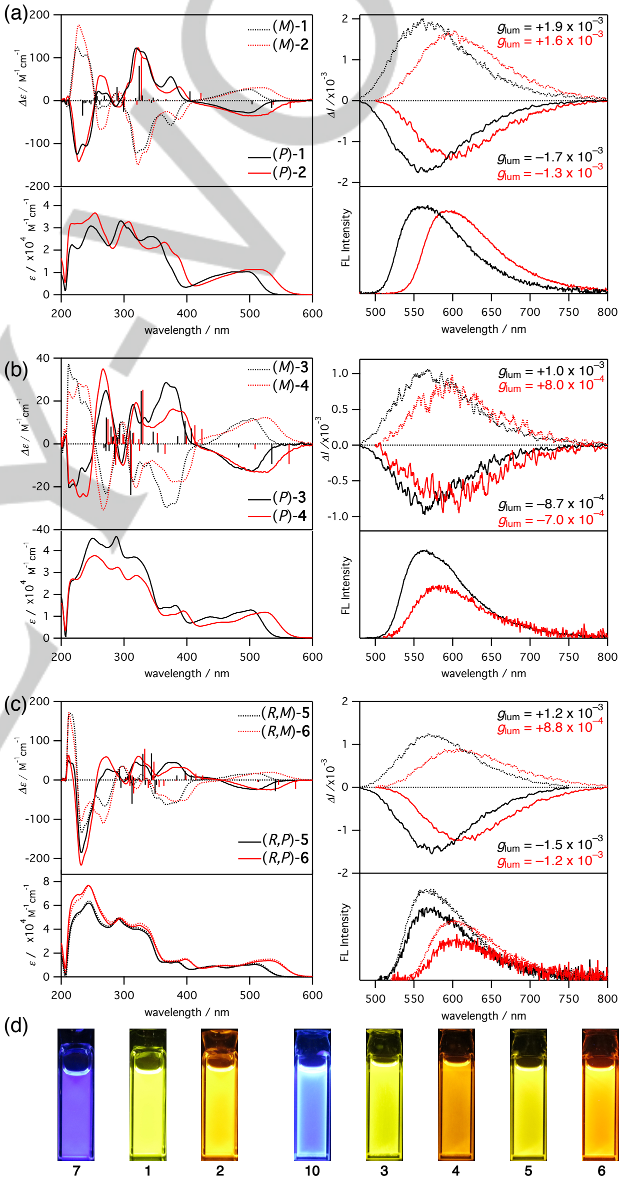

Figure 3. CD, UV/vis, CPL, FL spectra of (a) **1** and **2**, (b) **3** and **4**, and (c) **5** and **6** in 1,4-dioxane. Rotatory strengths of (*P*)-enantiomers/diastereomers are inserted in the spectra. (d) Photographs of 1,4-dioxane solutions of **1**–**7** and **10** under black light (λ = 365 nm).

The chiroptical properties of optically pure azahelicene-based dyes **1**–**6** were investigated (Figure 3 and Table 1). The UV-vis absorption spectra showed bands at 200–400 and 400–550 nm, which are more red-shifted as compared to the parent aza[7]helicenes such as **10** (411 nm). The CD spectra of enantiomers of **1**–**4** showed mirror images. On the other hand, the diastereomers of **5** and **6** showed negative split CD around 230 nm for the (*R*)-binaphthyl and nearly mirror images at 350–550 nm. The $|g_{abs}|$ values are 1.1×10^{-3}–3.1×10^{-3} at the longest absorption maxima (ca. 500 nm). They showed fluorescence in the visible region with the quantum yields of 0.20–0.36.[13] In addition, CPL was also observed in the same region with the $|g_{lum}|$ values of 7.0×10^{-4}–1.9×10^{-3}. The higher $|g_{lum}|$ values in comparison to the previously reported nonhelicenic dyes with a binaphthyl unit (3.0×10^{-4}–5.2×10^{-4}) are probably ascribed to the CPL ability of the [7]helicene framework superior to that of the binaphthyl group.[10e,14] Interestingly, the chiroptical properties of helical chirality were enhanced by the attachment of axial chirality. Specifically, **5** and **6** showed more intense Cotton effect and CPL than **3** and **4**, respectively. In addition, (*R*,*P*)-**5** and (*R*,*P*)-**6** showed more intense Cotton effect and CPL than (*R*,*M*)-**5** and (*R*,*M*)-**6**, which suggests that the (*P*)-aza[7]helicene moiety and (*R*)-binaphthyl group enhanced the effect of chirality. We then investigated the chiroptical properties of **10** to evaluate the g_{abs} and g_{lum} values of **3**–**6**. Optical resolution of **10** was achieved by the diastereomer method (SI), and CD and CPL of enantiomerically pure **10** were measured. The g_{abs} and g_{lum} values of (*P*)-**10** are -1.8×10^{-3} at 411 nm and -1.9×10^{-3} at 428 nm, respectively, which are comparable to those of **3**–**6**. This result indicates that **3**–**6** have effective π-extension without significant loss of chirality of the azahelicene moieties, which allows the distinct CPL reaching the NIR region. Considering the facile synthesis of **3**–**6** and the chiroptical properties comparable to **1** and **2**, triphenylene-based aza[7]helicene **10** is a useful platform for helical CPL dyes including **3**–**6**.

Table 1. Chiroptical properties in 1,4-dioxane

compd	λ_A [nm]	g_{abs}[a]	λ_F [nm]	Φ_F	g_{lum}[b]
(*P*)-**1**	495	-2.7×10^{-3}	568[c]	0.218	-1.7×10^{-3}[g]
(*P*)-**2**	508	-3.1×10^{-3}	594[d]	0.200	-1.3×10^{-3}[g]
(*P*)-**3**	508	-1.2×10^{-3}	566[d]	0.330	-8.7×10^{-4}[g]
(*P*)-**4**	524	-1.1×10^{-3}	592[e]	0.210	-7.0×10^{-4}[h]
(*R*,*P*)-**5**	508	-2.3×10^{-3}	576[d]	0.296	-1.5×10^{-3}[g]
(*R*,*M*)-**5**	509	$+1.5 \times 10^{-3}$	571[d]	0.364	$+1.2 \times 10^{-3}$[g]
(*R*,*P*)-**6**	530	-1.8×10^{-3}	605[e]	0.204	-1.2×10^{-3}[h]
(*R*,*M*)-**6**	532	$+1.5 \times 10^{-3}$	602[e]	0.265	$+8.8 \times 10^{-4}$[h]
(*P*)-**10**	411	-1.8×10^{-3}	428[f]	0.310	-1.9×10^{-3}[f]

[a] $g_{abs} = \Delta\varepsilon/\varepsilon$ at λ_A. [b] $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$. Average value in the range of $\lambda_F \pm 10$ nm. [c] Excited at λ = 460 nm. [d] Excited at λ = 480 nm. [e] Excited at λ = 500 nm. [f] Excited at λ = 320 nm. [g] Excited at λ = 360 nm. [h] Excited at λ = 400 nm.

DFT calculations were performed to investigate the molecular orbitals (Figure 4 and S8 in SI).[15] HOMO and LUMO of **1**–**4** have electronic coefficients mainly at the aza[7]helicene moieties and benzoazole moieties, respectively. This trend is also seen for **5** and **6**, while small contributions at the binaphthyl moieties were observed for the HOMO. These results suggest intramolecular charge transfer (ICT) from the azahelicene moiety to the BODIPY framework, which is responsible for the CD and CPL in the visible region.[4f,8m] In addition, ICT from the chiral binaphthyl units may contribute to the enhancement of CPL of **5** and **6**.[16] Thus the results of DFT calculations are consistent with the experimental chiroptical properties.

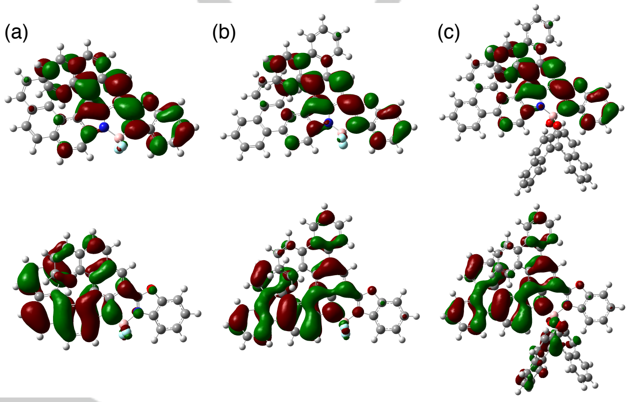

Figure 4. HOMO (bottom) and LUMO (top) of (a) (*P*)-**1**, (b) (*P*)-**3**, and (c) (*P*)-**5** calculated at the B3LYP/6-31G* level.

In summary, we have synthesized helical carbazole-based BODIPY analogs **1**–**6** via aza[7]helicenes **7** and **10**. π-Extended azahelicene **10** was readily synthesized for the first time in 90% yield in 2 steps from commercially available 3,6-dibromocarbazole. The novel azahelicene **10** was characterized by X-ray diffraction analysis, and **10** showed CPL in a blue region with g_{lum} of -1.9×10^{-3}. **7** and **10** were further converted into helical carbazole-based boron complexes **1**–**6**. X-ray crystal structures of **2** and **3** revealed the structures of azahelicene-incorporated BF_2 dyes. As a result of π-extended chiral conjugated system, **1**–**6** showed red-shifted CPL. Attachment of the axially chiral binaphthyl to helically chiral **3** and **4** improved the chiroptical properties of **5** and **6**. Further development of chiral carbazole-based boron complexes and azahelicene-based chiral dyes are currently underway in our laboratory.

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Keywords: carbazoles • helicenes • circularly polarized luminescence • BODIPY • dyes/pigments

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[11] a) Crystal data for **2**: Formula: $C_{35}H_{19}N_2SBF_2$, M_w = 548.39, monoclinic , space group $C\ 2/c$, a = 28.920(8), b = 10.056(3), c = 20.328(8) Å, β = 92.522(9)°, V = 5906(3) Å^3, Z = 8, ρ_{calcd} = 1.234, T = –180 °C, 35078 measured reflection, 4751 unique reflections (R_{int} = 0.1197), R_1 = 0.0984, $_wR_2$ = 0.2905 (all data), GOF = 1.038; b) Crystal data for **10**: Formula: $C_{36}H_{21}N$, M_w = 467.54, monoclinic , space group $P\ 2_1/a$, a = 12.156(2), b = 13.5034(15), c = 13.738(2) Å, β = 98.885(4)°, V = 2227.9(5) Å^3, Z = 4, ρ_{calcd} = 1.394, T = –180 °C, 30306 measured reflection, 4439 unique

reflections (R_{int} = 0.0223), R_1 = 0.0390, $_{\mathrm{w}}R_2$ = 0.1182 (all data), GOF = 1.024; c) Crystal data for **3**: Formula: $C_{43}H_{23}N_2OBF_2\cdot 1.5(C_6H_5Cl)$, M_{w} = 801.27, triclinic, space group *P*–1, *a* = 8.8018(15), *b* = 13.706(2), *c* = 16.431(5) Å, α = 78.63(2), β = 89.34(3), γ = 73.00(2)°, *V* = 1856.1(8) Å^3, *Z* = 2, ρ_{calcd} = 1.434, *T* = –180 °C, 21023 measured reflection, 5692 unique reflections (R_{int} = 0.0438), R_1 = 0.0963, $_{\mathrm{w}}R_2$ = 0.2594 (all data), GOF = 1.032. CCDC 1976458 (**2**), 1976459 (**10**), and 1976460 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystal Data Centre via www.ccdc.cam.au.uk/data_request/cif.

[12] The HOMO of **9** exhibited large electronic coefficients at the 4- and 5-positions of carbazole but no coefficients at the 2- and 7-positions, which supports the selective synthesis of **10** (Figure S7 in SI).

[13] We investigated the solvent effect on the fluorescence quantum yield of **3** (Figure S4 in SI).

[14] Related [7]helicenes also showed comparable g_{lum} values.[4e]

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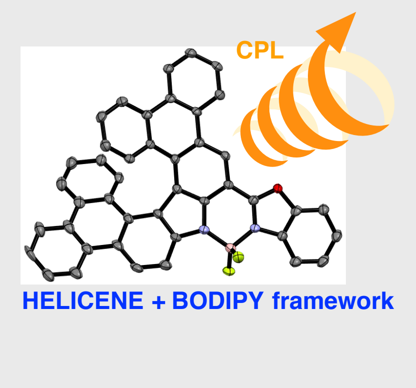
[16] The aza[7]helicene moieties of the optimized structures of (*P*)-**3** and (*R*,*P*)-**5** are quite similar, and ICT is more plausible than a simple chiral perturbation exerted by the BINOL moiety on the chiral helicenic chromophore.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Helical carbazole-based boron complexes were readily synthesized via aza[7]helicenes. The π-conjugated system expanded from the helicene moiety to the BODIPY framework, and the azahelicene-fused boron complexes showed the Cotton effects and the distinct circularly polarized luminescence (CPL) in the visible region.



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