A Facile Synthesis of Chiral Luminescent Organoboron Polymers by Hydroboration Polymerization Utilizing Chiral Borane

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ABSTRACT: Hydroboration polycondensations of three aromatic dicyano compounds **1**, 1,4-dicyanobenzene (**1a**), 1,3-dicyanobenzene (**1b**), and 1,4-didodecyloxy-2,5-dicyanobenzene (**1c**), with *N,N,N′,N′*-tetramethylethylenediamine-bis(monoisopinocampheylborane) (*S*-IpcBH$_2$·TMED) were carried out to obtain optically active poly(cyclodiborazane)s (**2a**, **2b**, and **2c**) with M_ns in the range from 2400 to 6800 in 61−76% yields. The hydroboration polycondensation efficiently proceeded through the complete formation of boron−nitrogen four-membered ring. The polymer structures were characterized by ^{1}H and ^{11}B NMR, UV−vis, photoluminescence (PL), and CD spectroscopies. Only **2c** exhibited intense blue-green light emission from charge-transfer interaction by incorporation of donor and acceptor system into the polymer backbone. The emission behavior of model compounds (**A** and **B**), corresponding to polymer units of **2a** and **2c**, was effectively examined by theoretical calculations using the DFT method. As a result, the intense blue-green emission of **2c** was observed by the bathochromic shift to a visible region. All the polymers showed intense CD signals, indicating that they formed chiral boron−nitrogen four-membered ring structure. Further, **3b** and **3c** were prepared by hydroboration polycondensation of **1b** or **1c** with *R*-IpcBH$_2$·TMED. The specific rotations of **2a**, **2b**, and **2c** showed positive values in contrast to those of **3b** and **3c**. The Cotton effects of the cyanobenzene moieties in **2a**, **2b**, and **2c** at around 300−350 nm were positive, whereas the Cotton effects of the cyanobenzene moieties in **3b** and **3c** were negative, as were the specific rotations as well.

Introduction

In the past decades, considerable interest has been devoted to the design, synthesis, and characterization of chiral π-conjugated oligomers and polymers directed at the formation of helices, twisted ribbons, and cholesteric mesomorphism both in solution and in neat films.[1] In addition, there is also the hope that chiral polymers may have an application in areas such as the development of circularly polarized photo- and electroluminescent materials and enantioselective sensors and/or catalysts.[2] Although some positive reports have been achieved from developing electron-rich p-type π-conjugated polymers carrying chiral pendants including poly(thiophene),[3] polyfluorene,[4] poly(*p*-phenylene),[5] polycarbazole,[6] poly(*p*-phenyleneethynylene),[7] poly(*p*-phenylenevinylene),[8] poly(dithienopyrrole),[9] and poly(acetylene)[10] derivatives, only poly(*m*-ethynylpyridine)s as electron-deficient n-type π-conjugated polymers possessing helical structures have been reported.[11] Recently, we have investigated the synthesis of n-type π-conjugated organoboron polymers, which presented unique properties such as intense blue emission and excellent third-order nonlinear optical properties, by hydroboration polymerization of aromatic diynes[12] and dicyano compounds.[13] Therein, poly(cyclodiborazane)s consisting of boron−nitrogen four-membered rings are also easily prepared by hydroboration polymerization of dicyano compounds, and they also showed good stability toward air and moisture. Further, fully aromatic poly(cyclodiborazane)s could be also regarded as π-conjugated organoboron polymers. Because incorporation of donor and acceptor units in the polymer main chain brought about a dramatic change in the electronic structure,[14] the preparation of poly(cyclodiborazane)s from dicyano-oilgothiophenes with different numbers of thiophene repeating units showed various light-emitting colors.[15] These prompted us to explore optically active n-type π-conjugated organoboron polymers. Therefore, we selected a chiral monoisopinocamphenylborane (IpcBH$_2$) derived from α-pinene as a candidate of a chiral monomer, which is a well-known chiral hydroborating reagent for asymmetric synthesis of amines,[16] halides,[17] ketones,[18] hydrocarbons,[19] and alcohols;[20] i.e., if IpcBH$_2$ is employed as the monomer of hydroboration polymerization of aromatic dicyano compounds, we should be able to obtain optically active poly(cyclodiborazane)s. Herein, this article deals with the hydroboration polymerization of aromatic dicyano compounds using chiral borane and the optical and chiroptical properties of the obtained polymers.

Experimental Section

Materials. 1,4-Dicyanobenzene (Wako Chemical, Co., 98%) and 1,3-dicyanobenzene (Wako Chemical, Co., 98%), *S*-alpine−boramine (*S*-IpcBH$_2$·TMED) (Aldrich Chemical, Co.), *R*-alpine−boramine (*R*-IpcBH$_2$·TMED) (Aldrich Chemical, Co.), and bis[2-(2-methoxyethoxy)ethyl] ether (diglyme) (Wako Chemical, Co., 95%) were used as received. 1,4-Didodecyloxy-2,5-dicyanobenzene was prepared according to the reported procedure.[21]

Hydroboration Polycondensation of 1,4-Dicyanobenzene with *S*-Alpine−Boramine (2a). Typical Procedure. Diglyme (0.2 mL) and 1,4-dicyanobenzene (0.032 g, 0.25 mmol) were subsequently introduced to a polymerization tube containing *S*-IpcBH$_2$·TMED (0.10 g, 0.25 mmol). After the resulting mixture was stirred at 100 °C for 24 h under nitrogen, the resulting mixture was poured into methanol (200 mL) to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. **2a** was obtained as a colorless solid. Yield = 61%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.35−2.62 (monoisopinocampheyl, 34H), 7.23−8.12 (C$_6$*H*$_4$, 4H), 8.23−8.40 (−C*H*=N−, 2H) ppm. ^{11}B NMR (CD$_2$Cl$_2$): δ = 1.86 and 33.0 ppm. IR (KBr): ν = 2360 (B−H), 1651 (C=N) cm^{-1}. Anal. Calcd for $(C_{28}H_{42}B_2N_2)_n$: C, 78.53; H, 9.88; B, 5.05; N, 6.54. Found: C, 78.67; H, 8.99.

2b. Colorless solid. Yield = 72%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.52−2.65 (monoisopinocampheyl, 34H), 7.12−8.33 (C$_6$*H*$_4$, 4H), 8.34−8.61 (−C*H*=N−, 2H) ppm. ^{11}B NMR (CD$_2$Cl$_2$): δ = 3.71 and 33.1 ppm. IR (KBr): ν = 2360 (B−H), 1652 (C=N) cm^{-1}.

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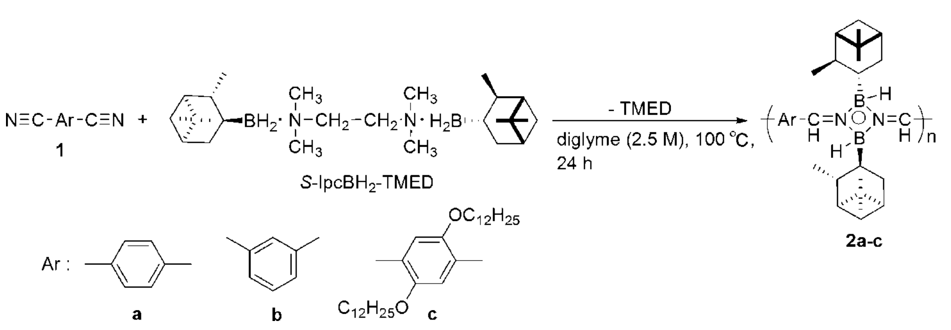
Scheme 1. Hydroboration Polymerization of Aromatic Dicyano Monomers 1a−c with *S*-IpcBH$_2$-TMED



Anal. Calcd for $(C_{28}H_{42}B_2N_2)_n$: C, 78.53; H, 9.88; B, 5.05; N, 6.54. Found: C, 78.58; H, 9.07.

2c. Viscous yellow oil. Yield = 76%. ^{1}H NMR (CD_2Cl_2): δ = 0.72−2.98 (monoisopinocampheyl and $CH_3(CH_2)_{10}CH_2O-$ × 2, 80H), 3.80−4.12 ($CH_3(CH_2)_{10}CH_2O-$ × 2, 4H), 6.72−7.02 (C_6H_2, 1H), 7.23−7.78 (C_6H_2, 1H), 8.61−8.92 (−C*H*═N−, 2H) ppm. ^{11}B NMR (CD_2Cl_2): δ = 2.05 ppm. IR (KBr): ν = 2359 (B−H), 1645 (C═N) cm^{-1}. Anal. Calcd for $(C_{52}H_{90}B_2N_2O_2)_n$: C, 78.37; H, 11.38; B, 2.71; N, 3.52. Found: C, 77.02; H, 10.72.

Hydroboration Polycondensation of 1,4-Dicyanobenzene with *R*-Alpine−Boramine (3b). Typical Procedure. Diglyme (0.2 mL) and 1,4-dicyanobenzene (0.032 g, 0.25 mmol) were subsequently introduced to a polymerization tube containing *R*-IpcBH$_2$·TMED (0.10 g, 0.25 mmol). After the resulting mixture was stirred at 100 °C for 24 h under nitrogen, the resulting mixture was poured into methanol (200 mL) to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. **3b** was obtained as a colorless solid. Yield = 69%. ^{1}H NMR (CD_2Cl_2): δ = 0.43−2.60 (monoisopinocampheyl, 34H), 7.16−8.31 (C_6H_4, 4H), 8.32−8.54 (−C*H*═N−, 2H) ppm. ^{11}B NMR (CD_2Cl_2): δ = 4.10 and 33.2 ppm. IR (KBr): ν = 2360 (B−H), 1651 (C═N) cm^{-1}. Anal. Calcd for $(C_{28}H_{42}B_2N_2)_n$: C, 78.53; H, 9.88; B, 5.05; N, 6.54. Found: C, 78.56; H, 9.22.

3c. Viscous yellow oil. Yield = 82%. ^{1}H NMR (CD_2Cl_2): δ = 0.67−2.68 (monoisopinocampheyl and $CH_3(CH_2)_{10}CH_2O-$ × 2, 80H), 3.82−4.14 ($CH_3(CH_2)_{10}CH_2O-$ × 2, 4H), 6.55−7.13 (C_6H_2, 1H), 7.32−7.80 (C_6H_2, 1H), 8.62−8.93 (−C*H*═N−, 2H) ppm. ^{11}B NMR (CD_2Cl_2): δ = 1.56 and 32.9 ppm. IR (KBr): ν = 2360(B−H), 1638 (C═N) cm^{-1}. Anal. Calcd for $(C_{52}H_{90}B_2N_2O_2)_n$: C, 78.37; H, 11.38; B, 2.71; N, 3.52. Found: C, 78.02; H, 10.99.

Synthesis of Model Compound 4. *S*-IpcBH$_2$·TMED (0.10 g, 0.25 mmol) was added to a solution of benzonitrile (0.41 mL, 6.0 mmol) in diglyme (4.0 mL), and the resulting mixture was stirred at 100 °C for 24 h under nitrogen. After that, the resulting mixture was poured into hexane (100 mL) to precipitate a product. The product was purified by silica gel column chromatography eluted with $CHCl_3$/hexane (1/4 = v/v) gave **4** as a colorless solid. Yield = 85%. ^{1}H NMR (CD_2Cl_2): δ = 0.44−2.22 (monoisopinocampheyl, 34H), 7.44−7.48 (6H, $-C_6H_5$ × 2), 7.80−7.88 (4H, $-C_6H_5$ × 2), 8.36 (2H, −C*H*═N〈) ppm. ^{11}B NMR (CD_2Cl_2): δ = 3.52 and 33.1 ppm. Anal. Calcd for $C_{34}H_{48}B_2N_2$: C, 80.64; H, 9.55; B, 4.27; N, 5.53. Found: C, 80.39; H, 9.32.

Instrumentation. ^{1}H (400 MHz) and ^{11}B (128 MHz) spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H NMR spectra used tetramethylsilane (TMS) as an internal standard in CD_2Cl_2, and ^{11}B NMR spectra were referenced externally to $BF_3·OEt_2$ (sealed capillary). The number-average molecular weights (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size exclusion chromatography (SEC) with a TOSOH G3000HXI system equipped with a polystyrene gel column [TOSOH gel: α-4000] and refractive index and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min with a tetrahydrofuran as an eluent. Polystyrene standards were employed for calibration. UV−vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence emission spectra were measured on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in THF (1.0 × 10^{-5} mol/L), and the absolute quantum yields were measured by integrating sphere method on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in THF (1.0 × 10^{-5} mol/L). FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-820 spectropolarimeter with THF as a solvent. Specific rotations ($[\alpha]_{25}{}^{D}$) were measured with a RUDOLPH RESEARCH ANALYTICAL ATUTOPOL IV digital polarimeter.

Results and Discussion

The chiral borane monomer, *N,N,N′,N′*-tetramethylethylenediamine-bis(monoisopinocampheylborane) (*S*-IpcBH$_2$·TMED), as *S*-alpine−boramine is currently commercially available. The polymers were prepared by the hydroboration polycondensations of three aromatic dicyano compounds, 1,4-dicyanobenzene (**1a**), 1,3-dicyanobenzene (**1b**), and 1,4-didodecyloxy-2,5-dicyanobenzene (**1c**),[21] using *S*-IpcBH$_2$·TMED in diglyme (2.5 mol/L) at 100 °C at [M]/[S-IpcBH$_2$·TMED] = 1 for 24 h (Scheme 1). After polymerization, the polymers were precipitated in methanol and collected under air and moisture in 61−76% yields. The size-exclusion chromatography (SEC) in tetrahydrofuran (THF) toward polystyrene standards revealed the weight-average molecular weights (M_w) and the number-average molecular weights (M_n) of 4800 and 2400, 10 000 and 3800, and 17 700 and 6800 g/mol (**2a**, **2b**, and **2c**, respectively) and polydispersity (M_w/M_n) of 2.01, 2.64, and 2.60 (**2a**, **2b**, and **2c**, respectively). The degrees of polymerization (DPs) estimated by M_n from SEC were 5.6, 8.9, and 8.5 (**2a**, **2b**, and **2c**, respectively). These obtained polymers were soluble in a variety of common solvents including chloroform ($CHCl_3$), THF, dichloromethane (CH_2Cl_2), benzene, and *N,N*-dimethylformamide (DMF). According to the previous works,[12−15] the structures of the corresponding polymers was confirmed by ^{1}H, ^{11}B NMR, and IR spectroscopies. For example, in the ^{1}H NMR spectrum of **2a**, the protons corresponding to monoisopinocampheyl group were observed at 0.35−2.62 ppm, and the peak at 8.12−8.42 ppm was assigned to imino proton (C*H*═N). The ^{11}B NMR spectrum of **2a** showed the main peak at 1.86 ppm, indicating the formation of cyclodiborazane units, and the minor peak at 33.03 ppm, ascribing monomeric iminoborane at the end group. In the IR spectrum, a strong peak due to the C═N stretching band was observed at 1650 cm^{-1}. The peak of C≡N, which was observed at 2240 cm^{-1} in the spectrum of monomer **1a**, was not observed in the spectrum of **2a**, indicating the complete conversion of C≡N; i.e., the hydroboration polycondensation efficiently proceeded through the complete formation of boron−nitrogen four-membered ring. However, it was difficult to control the regioregularity such as *cis*- and *trans*-conformation regarding the C═N bond in the obtained polymers.[13a]

Information for the optical properties of the obtained polymers was given by the UV−vis and photoluminescence (PL) mea-

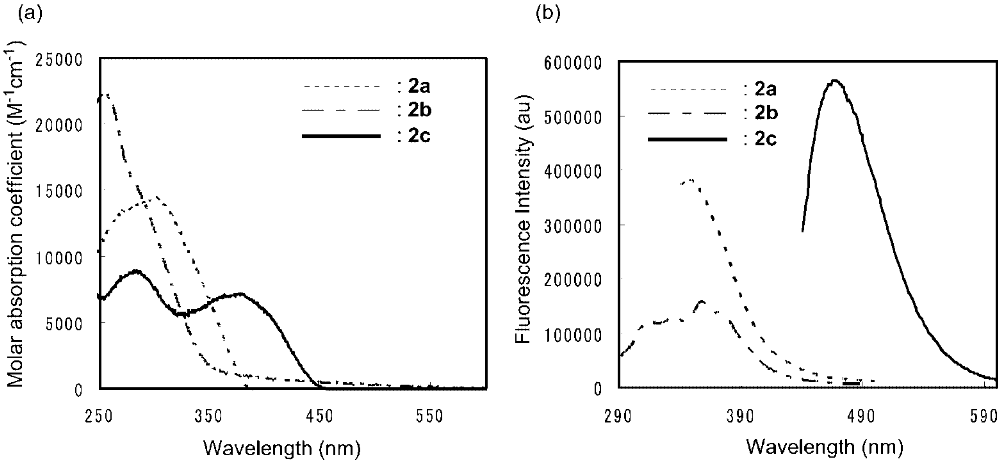


Figure 1. (a) UV−vis absorption and (b) fluorescence emission spectra of **2a**, **2b**, and **2c** in THF (1.0 × 10^{-5} mol/L).

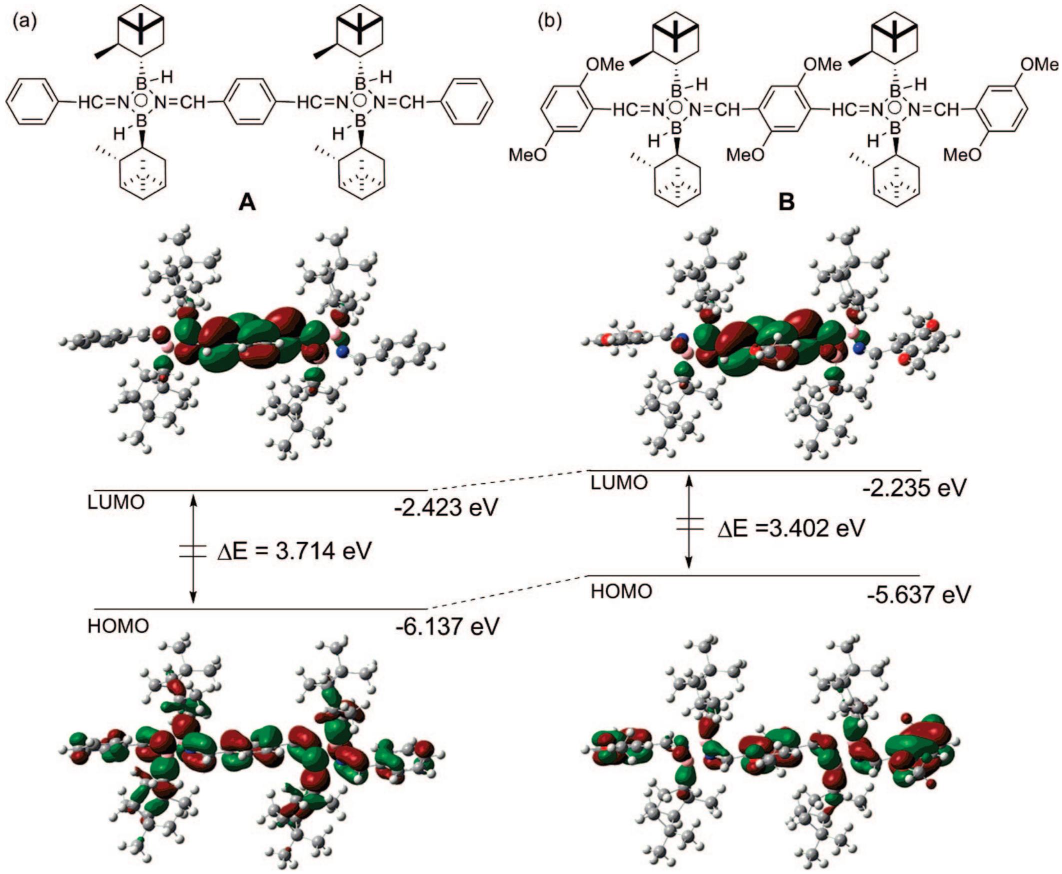


Figure 2. Trans-conformational structures and molecular orbital diagrams for the LUMO and HOMO of **A** (a) and **B** (b) (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)).

surements. The absorption maxima (λ_{max}) of *para*-linked polymer **2a** (λ_{max} = 300 nm) are red-shifted as compared to that of *meta*-linked polymer **2b** (λ_{max} = 253 nm), and the λ_{max} of **2c** exhibited a larger bathochromic shift than that of **2a** (λ_{max} = 376 nm) (Figure 1a). Further, the values of the molar absorption coefficients (ε) of the obtained polymers were in an order of **2b** > **2a** > **2c**. The possible reasons for the red shift and molecular absorption coefficients are (1) the presence of some intramolecular charge-transfer interaction and/or (2) interunit conjugation along the polymer backbone; i.e., the relationship between **2a** and **2b** is the difference of π-conjugated length in the dicyanobenzene moieties of *para*- and *meta*-substituents, and the highest occupied molecular orbital (HOMO) of **2c** is higher than that of **2a** by alkoxy groups as electron-donating groups (discussion later). Figure 1b illustrates the photoluminescent (PL) emission spectra of **2a**, **2b**, and **2c** in dilute THF solutions, excited at absorption maxima. Although **2a** and **2b** showed emission maxima at 345 nm (excited at 300 nm) and 358 nm (excited at 253 nm), respectively, their visible emission was not observed. In contrast, **2c** exhibited intense blue-green light emission upon irradiation with ultraviolet light. When the THF solution of **2c** was excited at 300 nm, the fluorescence emission spectrum showed an intense emission peak in the visible blue-green region (λ_{max} = 468 nm). The absolute fluorescence quantum yield of **2c** in THF at room temperature was determined as $\Phi_F = 0.18$, meaning the emission from charge-transfer interaction by incorporation of donor and acceptor units into the polymer main chain.[14,15] In contrast, the

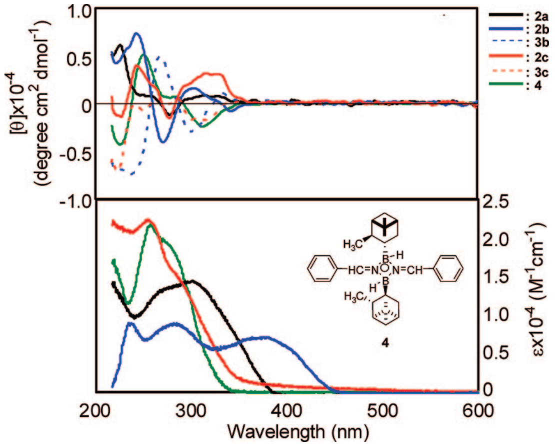


Figure 3. CD and UV−vis spectra (1.0×10^{-5} mol/L, THF) of **2a**, **2b**, **3b**, **2c**, **3c**, and **4**. The inset shows the molecular structure of model compound **4**.

Φ_Fs of **2a** and **2b** were 0.05 and 0.02, respectively, resulting from lower electronic density of cyclodiborazane moieties than that of **2c** having an electron-donating group.

To provide effective understanding for their optical properties, **A** and **B** were designed as the trans-conformational model compounds of **2a** and **2c** by using the Gaussian 03 suit of programs,[22,23] and their electronic states were examined by theoretical calculations using a density-functional theory (DFT) method at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory (Figure 2). The lowest unoccupied molecular orbital (LUMO) of **A** is mainly located on the polymer main chain, and the HOMO is localized not only on the polymer main chain but also on the monoisopinocampheyl groups. In contrast, the HOMO of **B** is not almost on the whole of monoisopinocampheyl groups but predominantly lies on the backbone by electron-donating group although the LUMO is almost similar. Further, the HOMO−LUMO gap of **A** (3.402 eV) was narrower than that of **B** (3.714 eV). These data support that uprising of the HOMO level of **B** leads to the larger red shift in UV−vis absorption by the electron-donating group. The efficient emission of **2c** depends on hybridized orbital of the monoisopinocampheyl group in the HOMO; i.e., the HOMO of **A** reaches to the monoisopinocamphenyl group of the boron atom due to lower occupied orbital as compared to that of **B**.[24]

To characterize the chiroptical properties of the obtained polymers, we evaluated the circular dichroism (CD) spectra and specific rotations ($[\alpha]^{25}_D$) of the polymers. Figure 3 illustrates the CD and UV spectra of **2a** (M_n = 2400 g/mol, M_w/M_n = 2.01, $[\alpha]^{25}_D$ = 102°, DP = 5.6), **2b** (M_n = 3800 g/mol, M_w/M_n = 2.55, $[\alpha]^{25}_D$ = 121°, DP = 8.9), **2c** (M_n = 6800 g/mol, M_w/M_n = 2.60, $[\alpha]^{25}_D$ = 168°, DP = 8.5), and, further, **3b** (M_n = 3600 g/mol, M_w/M_n = 2.55, $[\alpha]^{25}_D$ = −133°, DP = 8.4), **3c** (M_n = 5400 g/mol, M_w/M_n = 2.62, $[\alpha]^{25}_D$ = −155°, DP = 6.8), which were prepared from the hydroboration polycondensation of **1b** or **1c** with *R*-IpcBH$_2$·TMED in a similar manner, and model compound **4** ($[\alpha]^{25}_D$ = 82.1°), which was synthesized by the reaction of *S*-IpcBH$_2$·TMED and benzonitrile. The specific rotations ($[\alpha]^{25}_D$) of **2a**, **2b**, and **2c** showed positive values in contrast to those of **3b** and **3c**. In contrast, the $[\alpha]^{25}_D$ of **4** was negative value as compared to the polymers derived from *S*-IpcBH$_2$ and was smaller than those of all polymers. The Cotton effects of the cyanobenzene moieties in **2a**, **2b**, and **2c** at around 300−350 nm are positive, whereas the Cotton effects of the cyanobenzene moieties in **3b** and **3c** are negative, as are the specific rotations as well. Moreover, the absorption value of maximum molar ellipticity ($[\theta]_{max}$) of **4** was almost the same or barely smaller than those of all polymers. From these data, although **2** and **3** have each opposite structure, it was difficult to completely control regulated higher-order structure such as helix due to the contamination of *cis*- and *trans*-conformation in the polymers. Further, **2a** showed the $[\theta]_{max}$ at a wavelength 20 nm longer than the wavelength of **2b**, indicating that the *p*-dicyanobenzene moieties are more largely conjugated than *meta*-counterpart. However, the relative Cotton effects at around 230−350 nm in *meta*-linked **2b** and **3b** are larger than those in *para*-linked **2a**, **2c**, and **3c**. This finding means that the conformation of *para*-linked polymers are loosely distorted as compared to those of *meta*-linked ones.[25]

In summary, we have demonstrated the facile synthesis of optically active conjugated organoboron polymers by hydroboration polycondensation of aromatic dicyanobenzene compounds with *N,N,N′,N′*-tetramethylethylenediamine-bis(monoisopinocampheylborane) (*S*- or *R*-IpcBH$_2$·TMED) as chiral boranes and illustrated the emission behavior of the polymers by UV−vis and photoluminescence spectroscopies and theoretical calculation using density-functional theory (DFT). The studies on specific rotation and CD spectra suggest that the polycondensation of dicyanobenzene compounds with chiral boranes efficiently proceeded via introduction of chirality in the polymer backbone. As far as we know, this is the first finding of the designs of chiral conjugated organoboron polymers. Further detailed investigation on the chiroptical properties and regioregular control of chiral poly(cyclodiborazane)s is ongoing.

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(23) To examine influence of stereo-conformations for the emission behavior, **A** having trans−trans, cis−trans, and cis−cis conformations ($\mathbf{A}_{\text{trans−trans}}$, $\mathbf{A}_{\text{cis−trans}}$, and $\mathbf{A}_{\text{cis−cis}}$) regarding the C═N bond were designed as the model compounds of **2a** by using the Gaussian 03 suit of programs,[22] and their electronic states were examined by the DFT method at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. The LUMO and HOMO states of $\mathbf{A}_{\text{trans-trans}}$ having trans-trans conformation were in good agreement with those of $\mathbf{A}_{\textbf{cis-trans}}$ and $\mathbf{A}_{\textbf{cis-cis}}$. The HOMO-LUMO gaps of $\mathbf{A}_{\text{trans−trans}}$, $\mathbf{A}_{\text{cis−trans}}$, and $\mathbf{A}_{\text{cis−cis}}$ were 3.714, 3.705, and 3.703 eV, respectively. These results indicate that the stereo-conformations regarding C═N bond in the polymer backbone should not be responsible for their emission behavior.

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