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Luminescent chiral organoboron 8-aminoquinolate-coordination polymers

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We have successfully synthesized optically active organoboron aminoquinolate-based coordination polymers bearing the chiral side chain derived from L-alanine, and studied their optical behavior by UV–vis and photoluminescence spectroscopies. Higher absolute quantum yields (Φ_F) of the obtained polymers, measured by integrating sphere method, were observed with electron-withdrawing substituent ($\Phi_F = 0.80$) than with electron-donating substituent ($\Phi_F = 0.52$). The circular dichroism (CD) study in the mixed solvents of $CHCl_3$ and DMF showed that the secondary structures of the obtained polymers were stabilized by hydrogen-bonding interaction in the side chain. From concentration dependence on the CD spectra, the chirality of the obtained polymers originated from the nature of one molecule.

Keywords: boron; conjugated polymer; chirality; amino acid; photoluminescence

Introduction

Active current interests in light-emitting organoboron dyes encompass both biological and material sciences, as well as chemistry. Many fluorescent organoboron dyes have been used as chemical probes,[1] photosensitizers[2] and optical sensing[3] due to large molar extinction coefficients and two-photon absorption cross sections, high emission quantum yields and sensitivity to the surrounding medium.[4] Incorporation of them, including boron 8-aminoquinolate as electroluminescent chromophores into π-conjugated polymer main chains,[5] i.e. π-conjugated organoboron polymers, is more attractive for applications such as electroluminescent devices, organic field-effect transistors, photovoltaics, and so on.[6] Recently, designs of π-conjugated organoboron polymers can be prepared by three conceivable approaches: (i) cross-coupling reaction between organoboron dye having bis-iodo groups and diyne compounds;[5a,c–e] (ii) additional coordination to π-conjugated polymer linker by boron compound;[5b,f] and (iii) direct coordination of two ligand-functionalized compound with diborylated compounds.[5g] The approach (iii) was unattainable until Jäkle and coworkers recently succeeded in synthesis of π-conjugated organoboron quinolate polymers through boron-induced ether cleavage. Photoluminescence properties of these polymers can be tuned by varying the degree of conjugation of the linker between the quinolate groups.

With regard to functionalization of the organoboron dyes, boron 8-aminoquinolates are more attractive than boron 8-quinolinolate because the former can introduce an additional functional group by amide linkage. The organoboron dyes need stability in several environments, such as acid, base, heat and light. To give this stability to the boron complexes, we tested introduction of a chiral substituent by amide linkage to stabilize the polymer main chain coordinated boron complex; i.e. if it is possible to prepare π-conjugated organoboron complex-connected polymers carrying chiral side chain, the stability of polymer backbone will be enhanced by secondary interactions of not only π-stacking between polymer backbone but also chiral stacking between polymer side chains.[7] This strategy, in which the relationship between chirality and conjugation is stricter, is the construction of chiral polymers with stable and rigid structures, such as helical structure.[8]

A particularly interesting moiety with amide group for chiral induction is derived from amino acids.[9] The combination of π-stacking and hydrogen-bonding interactions favors a more rigid chiral conformation. Therefore, it seems that the chiral amide side chain leads to safe preparation and stability of π-conjugated organoboron coordination polymers. Herein, we wish to report novel synthesis of chiral organoboron coordination polymers exhibiting high fluorescence quantum yield.

Results and Discussion

Initially, the ligand *N*-hexanoyl-L-alanine-*N*′-5-iodo-8-quinolylamide (**4**) was prepared from 8-aminoquinoline as starting compound according to Scheme 1. The reaction of this ligand (**4**) with 4,4′-bis[bromo(phenyl)boryl]biphenyl, which was treated with bis(dibromoboryl)biphenyl[10] and trimethyl(phenyl)tin by a modification of a literature procedure,[11] produced an organoboron aminoquinolate-based monomer **6** bearing bis-iodo and amide groups (Scheme 2). Monomer **6** was obtained as a yellow powder in 24% yield. Tetracoordination state of the boron atom of **6** was confirmed by the ^{11}B-NMR spectrum in $CDCl_3$ ($\delta_B = 7.13$ ppm). The basic structure of **6** was also identified by ^{1}H-NMR, ^{13}C-NMR, IR and high-resolution mass spectroscopies. However, ^{1}H-NMR and ^{13}C-NMR spectra of **6** showed the presence of many multiple peaks attributable to diastereomers, which originate from the stereogenic borons.[5g]

The Sonogashira–Hagihara coupling polymerization of **6** was conducted with 1,4-diethynyl-2,5- dioctyloxybenzene or 1,4-diethynyl-2-(perfluorooctyl)-5-(trifluoromethyl)benzene in the

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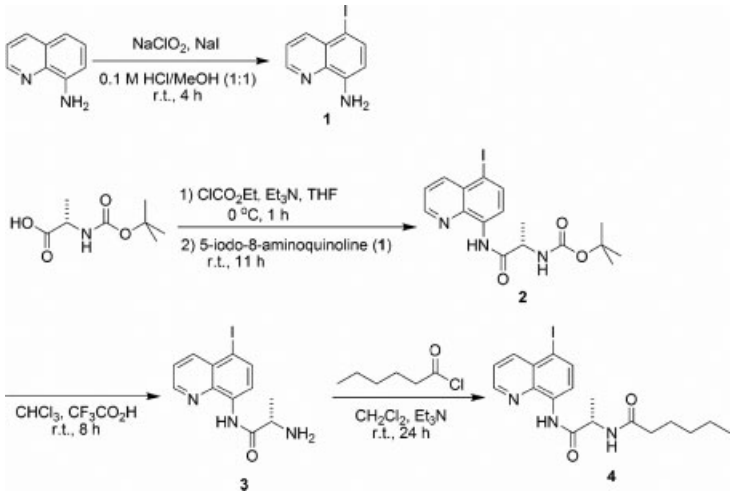
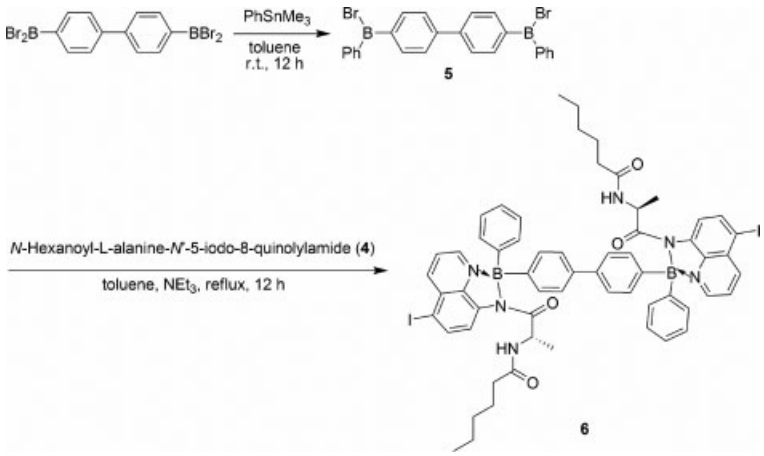


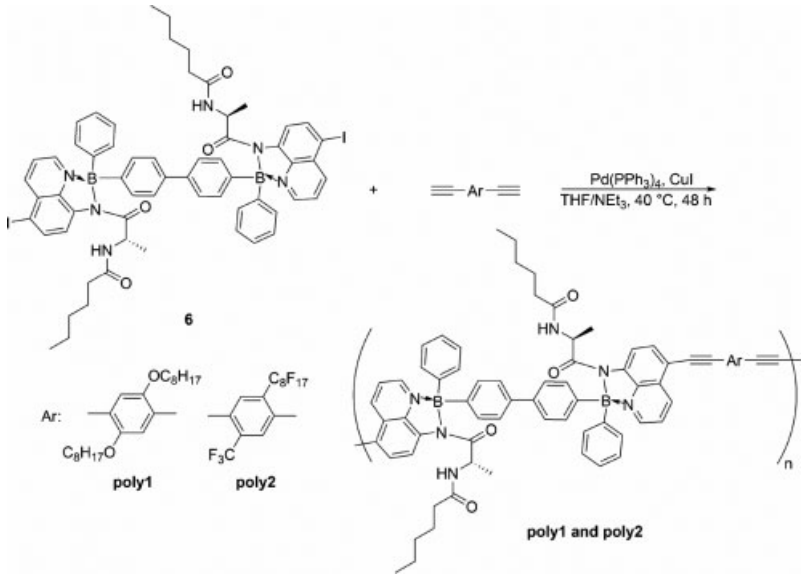
Scheme 1. Synthesis of *N*-hexanoyl-L-alanine-*N*′-5-iodo-8-quinolylamide.



Scheme 2. Synthesis of monomer **6**.

presence of $Pd(PPh_3)_4$ and CuI in the mixed solvent of tetrahydrofuran (THF) and triethylamine (NEt_3) at 40 °C for 48 h (Scheme 3). The obtained polymers **poly1** and **poly2** were collected as orange and yellow solids, respectively, after reprecipitation in methanol and in hexane. Their yields were 80 and 59%, respectively. The number-average molecular weights (M_n) and the molecular weight distributions (M_w/M_n) of **poly1** and **poly2**, measured by size-exclusion chromatography (SEC) in THF, were 5300 and 2.8, and 7900 and 3.1, respectively. The degrees of polymerization (DPs) estimated by M_n from SEC were 4.0 and 5.0 (**poly1** and **poly2**, respectively). The structures of the polymers were characterized spectroscopically. The ^{1}H, ^{11}B-NMR, ^{13}C-NMR and IR spectra of the polymers exhibited signals reasonably assignable to the structures illustrated in Scheme 3. For example, the IR spectra of the polymers showed the absorption peaks at around 2208 cm^{-1}, which are attributable to stretching of the –C≡C– bond in the polymer backbone, and the characteristic peaks at *c*. 4.40–6.35 ppm, which are assigned to tetracoordination state of the boron atom of the polymers, clearly seen by ^{11}B-NMR spectroscopy. These data indicate that the coupling reaction proceeded effectively without decomposition of the boron complex in the polymer main chain. The polymers were soluble in N,N-dimethylformamide (DMF), THF, $CHCl_3$ and CH_2Cl_2, and partly soluble in toluene, while insoluble in hexane, methanol and acetone.

UV–vis absorption spectra of monomer and the obtained polymers were recorded in $CHCl_3$ (1.0×10^{-5} mol l^{-1}) as shown in Fig. 1(a). The absorption bands of all compounds at *c*. 268–270 nm could be commonly assigned to the absorption of biphenyl unit in the polymer chain, corresponding to π–π^* transition. The monomer **6** showed the weak absorption band at 415 nm originating from the aminoquinoline ligand unit. In contrast to **6**, the absorption bands of both polymers (**poly1**, 461 nm, **poly2**, 446 nm) were red-shifted and significantly broadened to bathochomic side, and new bands of **poly1** and **poly2** appeared at 352 and 382 nm, respectively, attributable to *p*-phenylene–ethynylene units. The molar absorption coefficients (ε) of aminoquinoline moieties in the polymers (**poly1**: $\varepsilon = 0.38 \times 10^5$ M^{-1} cm^{-1}, **poly2**: $\varepsilon = 0.55 \times 10^5$ M^{-1} cm^{-1}) were higher than that in monomer (**6**: $\varepsilon = 0.12 \times 10^5$ M^{-1} cm^{-1}). These results indicate that π-conjugation lengths of the polymers were extended along the polymer backbone. Further, the absorption band of **poly1** was bathochromically shifted in comparison with that of **poly2**, while the ε of **poly2** was higher than that of **poly1**. These bathochromic shifts should be caused by the electronic structures of comonomers, i.e. donor–acceptor relation.[5d,12] Figure 1(b) illustrates the emission bands of **6, poly1**, and **poly2** in $CHCl_3$ (1.0×10^{-5} mol l^{-1}). The emission of **poly2** was green color at 509 nm (excited at 446 nm), while it was almost identical to that



Scheme 3. Cross-coupling reaction of monomer **6** with diyne compounds.

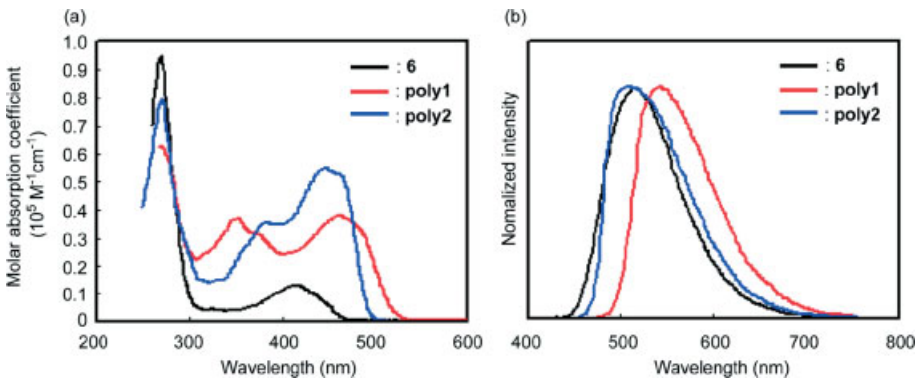


Figure 1. (a) UV–vis spectra of **6, poly1** and **poly2** in $CHCl_3$ (1.0×10^{-5} mol l^{-1}), and (b) normalized emission spectra of **6, poly1** and **poly2** in $CHCl_3$ (1.0×10^{-5} mol l^{-1}).

at 516 nm of **6** (excited at 415 nm). In contrast, the emission band of **poly1** was red-shifted to the bathochromic side as compared with those of **6** and **poly2** due to the highly electron-donating nature of the comonomer. Higher absolute quantum yields (Φ_F), measured by integrating sphere method, were observed with electron-withdrawing substituent (**poly2**: $\Phi_F = 0.80$) than that with electron-donating substituent (**poly1**: $\Phi_F = 0.52$),[12a] and **6** having bis-iodo groups on the aminoquinoline ligand displayed a lower Φ_F of 0.24 due to the internal heavy-atom effect.[13] These observations suggest that the substituents in the comonomers should be responsible for the intensity of fluorescence of the obtained polymers.

To confirm the secondary structures of the obtained polymers stabilized by hydrogen-bonding interaction, which is stimulated in polar solvents such as DMF, we carried out CD and UV–vis spectroscopic studies of **poly1** and **poly2** in the mixed solvent of $CHCl_3$–DMF as depicted in Fig. 2(a, b). In $CHCl_3$, the CD and UV–vis maxima of **poly1** were observed at 268, 352 and 461 nm, respectively, attributable to bisphenyl, *p*-phenylene-ethynylene and aminoquinoline units, respectively. Similarly, **poly2** also showed signals at 272 nm and at around 446 nm, at which both *p*-phenylene–ethynylene and aminoquinoline units were overlapped. These data indicate that the ordered secondary structures in the main chain are derived from chirality of amino acid moiety in the side chain, although it is difficult to completely control regulated higher-order structures such as helixes due to the contamination of the diastereomeric conformations in the polymers. The CD signals of the polymers gradually decreased by increasing the DMF content, suggesting stabilization by hydrogen-bonding interaction. In contrast, the specific rotations ($[\alpha]^{25}_D$) of the polymers in $CDCl_3$ and DMF were almost unchanged (**poly1**, -267° in $CHCl_3$ and -213° in DMF; and **poly2**, -264° in $CHCl_3$ and -279° in DMF). However, $[\alpha]^{25}_D$ of monomer **6** in $CHCl_3$ ($[\alpha]^{25}_D = -294^\circ$) was higher than that in DMF ($[\alpha]^{25}_D = -192^\circ$). These findings mean that the secondary structures of the obtained polymers were stabilized by stronger hydrogen-bonding interaction than that of the monomer. Next, the concentration dependence on the secondary structure of **poly1** was carried out in $CHCl_3$ (Fig. 3). Increasing the concentration leads to both bathochromic shifts and decrease in the CD effect, and the CD signal of **poly1** almost completely disappeared at 1.0×10^{-3} mol l^{-1}. The observed concentration dependence clearly shows that the observed Cotton effects are not due to supramoleuclar aggregation but due to the nature of one macromolecule. Figure 2(c, d) illustrates the emission spectra of the polymers in the mixed solvent of $CHCl_3$–DMF. Similarly to CD

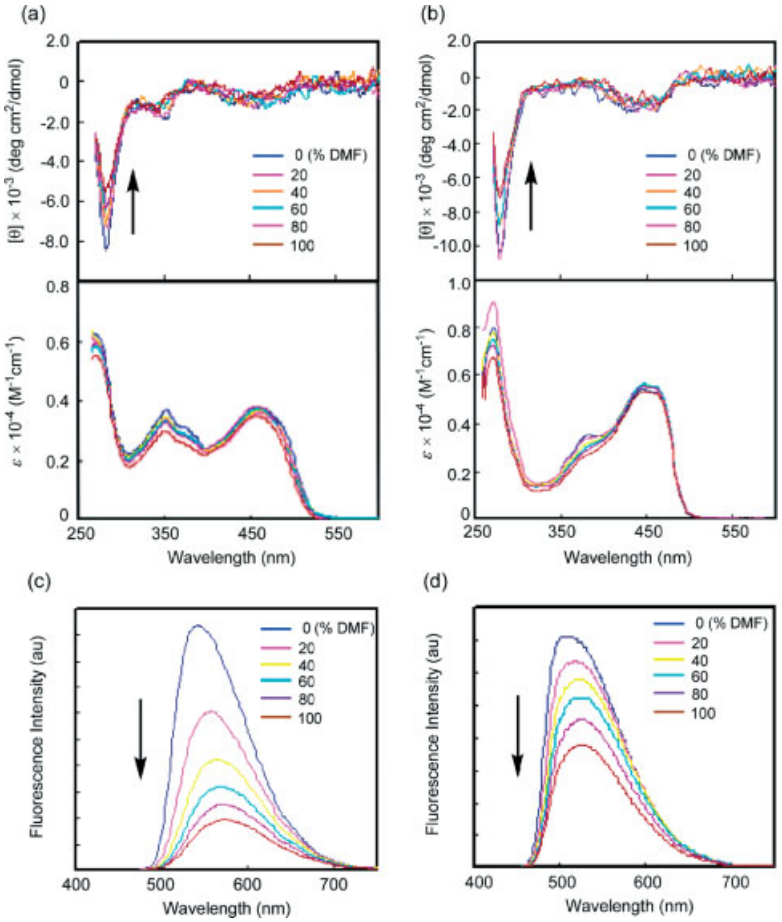


Figure 2. CD and UV-vis spectra of (a) **poly1** and (b) **poly2** in $CHCl_3$ and $CHCl_3$–DMF mixtures (1.0×10^{-5} mol l^{-1}), and emission spectra of (c) **poly1** and (d) **poly2** in $CHCl_3$ and $CHCl_3$–DMF mixtures (1.0×10^{-5} mol l^{-1}).

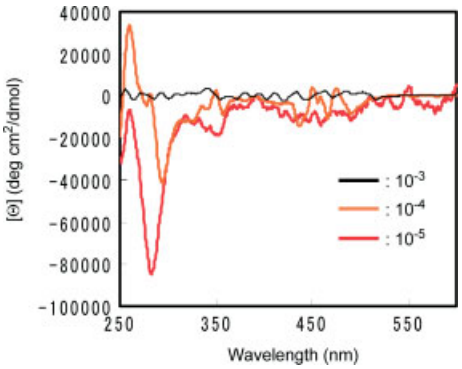


Figure 3. Concentration dependence in $CHCl_3$ of CD spectrum of **poly1**.

effects of the polymers in the mixed solvents, the emission spectra of the polymers also gradually decreased together with shifting to bathochromic side by increasing the DMF content, ruling out the possibility of effect on hydrogen-bonding interaction in the polymers. In other words, the red-shift and decrease of intensity in emission spectra mean that the excited state after intramolecular charge transfer (CT) is stabilized in the polar solvent. Further, the intensity of **poly1** with the electron-donating group greatly decreased in comparison with that of **poly2** having a electron-withdrawing group due to higher stabilization of the charge separated state,[14] and the Φ_F of **poly1** ($\Phi_F = 0.15$) was also smaller than that of **poly2** ($\Phi_F = 0.52$) in DMF.

Conclusions

We have successfully synthesized optically active organoboron aminoquinolate-based coordination polymers bearing the chiral side chain derived from L-alanine, and studied their optical behavior by UV–vis and photoluminescence spectroscopies. The dependence of the photoluminescence property on the solvent's polarity suggested the existence of intramolecular charge transfer. The CD study in the mixed solvents of $CHCl_3$ and DMF showed that the secondary structures of the obtained polymers were stabilized by hydrogen-bonding interaction in the side chain. The concentration dependence on the CD spectra demonstrated that the regulated higher-order structures of the obtained polymers are macromolecular in nature.

Experimental

General Procedures

^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz)-NMR spectra were recorded on a Jeol JNM-EX400 spectrometer. ^1H- and ^{13}C-NMR spectra used tetramethylsilane (TMS) as an internal standard, ^{11}B-NMR spectra were referenced externally to BF_3OEt_2 (sealed

capillary) in $CDCl_3$. 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 three consecutive polystyrene gel columns (TOSOH gels: α-4000, α-3000 and α-2500) and a UV detector at 40 °C. The system was operated at a flow rate of 1.0 ml min^{-1}, with 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 recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Preparation of the Compounds

1,4-Diethynyl-2,5-dioctyloxybenzene,[15] 4,4′-bis(dibromoboryl) biphenyl[16] and 1.4-diethynyl-2-perfluorooctyl-5-trifluoromethylbenzene[17] were prepared according to the literature. Tetrahydrofuran (THF) and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA, USA). Other reagents were commercially available and used as received.

*5-Iodo-8-aminoquinoline (**1**)*

A 0.1 M HCl (900 ml) aliquot was added to a solution of 8-aminoquinoline (13.0 g, 90.0 mmol), $NaClO_2$ (4.08 g, 45.0 mmol), and NaI (13.5 g, 90.0 mmol) in methanol, and the mixture was stirred at room temperature for 4 h. The precipitate was collected, and rinsed with aqueous $Na_2S_2O_3$ and water to afford 5-iodo-8-aminoquinoline in 68% yield (16.6 g, 61.4 mmol). ^{1}H-NMR ($CDCl_3$): δ = 5.07 (s, 2H, -N*H*$_2$), 6.72 (d, J = 8.0 Hz, 1H, quinoline ring, H$_7$), 7.45 (dd, J = 8.6, 4.1 Hz, 1H, H$_3$), 7.82 (d, J = 8.0 Hz, 1H, H$_6$), 8.27 (d, J = 8.6 Hz, 1H, H$_4$), 8.71 (d, J = 4.1 Hz, 1H, H$_2$) ppm. ^{13}C-NMR (DMSO-d_6): δ = 147.60, 146.43, 139.19, 138.23, 138.11, 129.45, 123.43, 110.41, 77.85 (Ar–I). Anal. calcd for $C_9H_7IN_2$: C, 40.03; H, 2.61; N, 10.37. Found: C, 40.14; H, 2.62; N, 10.35.

*N-(tert-Butoxycarbonyl)-L-alanine-N′-5-iodo-8-quinolylamide (**2**)*

N-(*tert*-Butoxycarbonyl)-L-alanine (3.41 g, 18.0 mmol) was dissolved in THF (90 ml), and triethylamine (2.50 ml, 18.0 mmol) and ethyl chlorocarbonate (1.72 ml, 18.0 mmol) were added to the mixture at 0 °C. After the mixture had been stirred at 0 °C for 1 h, 5-iodo-8-aminoquinoline was added. The reaction was continued at 0 °C for 1 h, and then stirred at room temperature for 11 h. The resulting mixture was filtered, and the filtrate was concentrated under vacuum. The crude product was purified by silica gel column chromatography eluted with hexane–ethyl acetate to give a brown solid in 73% yield (5.81 g, 13.2 mmol). ^{1}H-NMR ($CDCl_3$): δ = 1.49 (m, 12H, -C*H*$_3$), 4.51 (m, 1H, -C*H* →), 5.19 (m, 1H), 7.53 (dd, J = 8.6, 4.0 Hz, 1H, Ar–*H*), 8.07 (d, J = 8.3 Hz, 1H, Ar–*H*), 8.36 (d, J = 8.6 Hz, 1H, Ar–*H*), 8.53 (d, J = 8.3 Hz, 1H, Ar–*H*), 8.77 (d, J = 4.0 Hz, 1H, Ar–*H*), 10.36 (s, 1H, -N*H*–CO–CH→) ppm. ^{13}C-NMR ($CDCl_3$): δ = 171.37 (-NH–*C*O–CH→), 155.34 (-NH–*C*O–O-), 148.83 (Ar), 140.59 (Ar), 139.11 (Ar), 138.09 (Ar), 135.02 (Ar), 129.54 (Ar), 123.15 (Ar), 117.88 (Ar), 89.68 (Ar–I), 80.23 [-O–*C*(CH$_3$)$_3$], 51.33 (-*C*H →), 28.33 [-O–C(*C*H$_3$)$_3$], 18.55 (<CH–*C*H$_3$) ppm. IR(KBr): ν = 3320, 2972, 2929, 1695, 1506, 1368, 1315, 1248, 1160, 1101, 1061, 1028, 942, 912, 861, 832, 784, 750, 704, 639 cm^{-1}. HRMS: m/z, calcd for $C_{17}H_{20}IN_3O_3$: 441.0549; found: 441.0548 $[M]^+$. Anal. calcd for $C_{17}H_{20}IN_3O_3$: C, 46.27; H, 4.57; N, 9.52. Found: C, 46.25; H, 4.64; N, 9.44.

*Alanine-N′-5-iodo-8-aminoquinolylamide (**3**)*

N-(*tert*-Butoxycarbonyl)-L-alanine-*N*′-5-iodo-8-quinolylamide (5.00 g, 11.3 mmol) was treated with TFA (17 ml) in $CHCl_3$ (17 ml) for 32 h. An aliquot of 10% aqueous ammonia was added to the resulting mixture, followed by extraction with diethyl ether, drying over $MgSO_4$, and removal of the solvent to give a brown solid in 77.3% yield (2.98 g, 8.73 mmol). ^{1}H-NMR ($CDCl_3$): δ = 1.52 (d, J = 7.48 Hz, 3H, -C*H*$_3$), 1.87 (s, 2H, -N*H*$_2$), 3.78 (q, J = 6.96 Hz, -C*H* →), 7.53 (dd, J = 4.28 and 8.44 Hz), 8.07 (d, J = 8.32 Hz, 1H, Ar–*H*), 8.36 (dd, J = 8.56 and 1.48 Hz, 1H, Ar–*H*), 8.60 (d, J = 8.32 Hz, 1H, Ar–*H*), 8.83 (dd, J = 4.16 and 1.48 Hz, 1H, Ar–*H*), 11.43 (s, 1H, -N*H*–CO–CH→) ppm. ^{13}C-NMR ($CDCl_3$): δ = 174.61 (<*C*=O), 149.06 (Ar), 140.59 (Ar), 139.66 (Ar), 138.18 (Ar), 135.37 (Ar), 129.66 (Ar), 123.03 (Ar), 117.75 (Ar), 89.43 (Ar–I), 52.04 (-CH→), 21.77 (-C*H*$_3$) ppm. HRMS: m/z, calcd for $C_{12}H_{12}IN_3O$: 341.0025; found: 341.0030 $[M]^+$. Anal. calcd for $C_{12}H_{12}IN_3O_3$: C, 42.25; H, 3.55; N, 12.32. Found: C, 42.53; H, 3.71; N, 12.11.

*N-Hexanoyl-L-alanine-N′-5-iodo-8-quinolylamide (**4**)*

Alanine-*N*′-5-iodo-8-aminoquinolylamide (2.73 g, 8.00 mmol) and triethylamine (1.17 ml, 8.40 mmol) were dissolved in dichloromethane (36 ml), followed by addition of hexanoyl chloride (1.17 ml, 8.40 mmol). The resulting mixture was stirred at room temperature for 24 h. The mixture was transferred to a separating funnel and washed with aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$. Filtration and evaporation of the solvent gave a pale brown solid in 85.5% yield (3.01 g, 6.84 mmol). ^{1}H-NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, -CH$_2$–C*H*$_3$), 1.33 (m, 4H, -CH$_2$-), 1.56 (d, J = 7.1 Hz, 3H, <CH–C*H*$_3$), 1.68 (m, 2H, -CH$_2$-), 2.28 (t, J = 7.6 Hz, 2H), 4.86 (m, 1H, -C*H* →), 6.24 (d, J = 7.1 Hz, 1H, -N*H*–CO–CH$_2$-), 7.54 (dd, J = 8.6, 4.1 Hz, 1H, Ar–*H*), 8.07 (d, J = 8.3 Hz, 1H, Ar–*H*), 8.36 (d, J = 8.6 Hz, 1H, Ar–*H*), 8.48 (d, J = 8.3 Hz, 1H, Ar–*H*), 8.78 (d, J = 4.1 Hz, 1H, Ar–*H*), 10.20 (s, 1H, -N*H*–CO–CH→) ppm. ^{13}C-NMR ($CDCl_3$): δ = 173.97 (<*C*=O), 170.91 (<*C*=O), 149.06 (Ar), 140.73 (Ar), 139.02 (Ar), 138.08 (Ar), 134.91 (Ar), 129.60 (Ar), 123.29 (Ar), 118.00 (Ar), 89.92 (Ar–I), 49.77 (-CH→), 36.65, 31.42, 25.34, 22.39, 18.92, 18.82, 13.93 ppm. IR(KBr): ν = 3280, 3059, 2927, 2865, 1698, 1652, 1540, 1474, 1380, 1357, 1315, 1250, 1211, 1151, 1103, 1076, 1036, 961, 934, 908, 837, 785, 724, 694 cm^{-1}. HRMS: m/z, calcd for $C_{18}H_{22}IN_3O_2$: 439.0757; found: 439.0760 $[M]^+$. Anal. calcd for $C_{18}H_{22}IN_3O_2$: C, 49.21; H, 5.05; N, 9.57. Found: C, 49.38; H, 5.06; N, 9.52.

*Monomer (**6**)*

Trimethyl(phenyl)tin (4.78 ml, 26.3 mmol) was added to a solution of 4,4′-bis(dibromoboryl)biphenyl (6.49 g, 13.2 mmol) in toluene (263 ml) and the mixture was stirring for 14 h. All volatile components were removed under a high vacuum, and the crude product was washed with hexane. This product (1.17 g), *N*-hexanoyl-L-alanine-*N*′-5-iodo-8-quinolylamide (2.11 g, 4.80 mmol) and triethylamine (0.67 mll, 4.8 mmol) were dissolved in toluene (38 ml). After the reaction mixture had refluxed for 12 h, the solvent was removed by rotary evaporation. The residue was treated with water, followed by extraction with ethyl acetate, drying over $MgSO_4$ and removal of the solvent under vacuum. The crude products were purified by silica gel (neutral) column chromatography eluted with hexane–ethyl acetate.

Recrystallization from hexane–dichloromethane gave a yellow solid in 24% yield (0.70 g, 0.58 mmol). ^{1}H-NMR ($CDCl_3$): δ = 0.53 (6H, -CH_2–CH_3), 0.70 (1H), 0.86 (5H), 1.24 (8H, -CH_2-), 1.51 (4H, -CH_2-), 2.02 (4H, -CO–CH_2-), 4.71 (2H, -CH →), 6.18 (2H, -NH–CO–CH_2-), 7.27 (6H, Ar–H), 7.37 (4H, Ar–H), 7.52 (8H, Ar–H), 7.70 (2H, Ar–H), 8.26 (2H, Ar–H), 8.53 (4H, Ar–H), 8.72 (2H, Ar–H) ppm. ^{11}B-NMR ($CDCl_3$): δ = 7.13 ppm. ^{13}C-NMR ($CDCl_3$): δ = 177.00 (<C=O), 171.11 (<C=O), 143.50 (Ar), 143.39 (Ar), 142.34 (Ar), 142.24 (Ar), 141.95 (Ar), 140.88 (Ar), 140.73 (Ar), 140.14 (Ar), 140.07 (Ar), 139.84 (Ar), 138.18 (Ar), 134.69 (Ar), 134.59 (Ar), 134.29 (Ar), 132.74 (Ar), 132.57 (Ar), 132.29 (Ar), 129.60 (Ar), 128.07 (Ar), 127.65 (Ar), 127.50 (Ar), 126.71 (Ar), 126.58 (Ar), 126.46 (Ar), 123.99 (Ar), 123.93 (Ar), 120.76 (Ar), 120.63 (Ar), 83.48 (Ar–I), 50.31 (-CH→), 36.50, 31.28, 25.32, 22.40, 18.75, 13.96. IR(KBr): ν = 3418, 3331, 3070, 3045, 3006, 2954, 2926, 2855, 1645, 1578, 1575, 1504, 1462, 1393, 1307, 1276, 1192, 1145, 1114, 1070, 1022, 1003, 962, 882, 840, 818, 782, 738, 706, 666, 642 cm^{-1}. HRMS: m/z, calcd for $C_{60}H_{60}B_2I_2N_6O_4$: 1204.2952; found: 1204.2997 $[M]^+$. Anal. calcd for $C_{60}H_{60}B_2I_2N_6O_4$: C, 59.82; H, 5.02; N, 6.98. Found: C, 59.50; H, 4.88; N, 6.99.

Poly1

A typical procedure is shown as follows: triethylamine (0.70 ml) was added to a solution of **6** (0.170 g, 0.14 mmol), 1,4-diethynyl-2,5-dioctyloxybenzene (0.053 g, 0.140 mmol), $Pd(PPh_3)_4$ (8.10 mg, 7.00 μmol), CuI (2.60 mg, 14.0 μmol) in THF (1.40 ml) at room temperature. After the mixture had been stirred at 40 °C for 48 h, a small amount of $CHCl_3$ was added and poured into a large excess of methanol to precipitate the polymer. The polymer was purified by repeated precipitations from a small amount of $CHCl_3$ into a large excess of methanol and hexane respectively to give a red solid in 80.7% yield (0.15 g, 0.11 mmol). M_n = 5319. ^{1}H-NMR ($CDCl_3$): δ = 0.55 (6H, -CH_2–CH_3), 0.70 (1H), 0.86 (9H), 1.23(20H, -CH_2-), 1.37 (6H), 1.53 (8H, -CH_2-), 1.94 (4H, -CH_2-), 2.02 (4H, -CO–CH_2-), 4.12 (4H), 4.74 (2H, -CH →), 6.22 (2H, -NH–CO–CH_2-), 7.11 (2H, Ar–H), 7.29 (6H, Ar–H), 7.42 (4H, Ar–H), 7.55 (8H, Ar–H), 7.68 (2H, Ar–H), 8.02 (2H, Ar–H), 8.58 (2H, Ar–H), 9.05 (2H, Ar–H), 9.07 (2H, Ar–H) ppm. ^{11}B-NMR ($CDCl_3$): δ = 4.40 ppm. ^{13}C-NMR ($CDCl_3$): δ = 177.08 (<C=O), 171.17 (<C=O), 153.70 (Ar), 141.29 (Ar), 140.72 (Ar), 137.59 (Ar), 135.48 (Ar), 134.65 (Ar), 134.32 (Ar), 132.85 (Ar), 132.69 (Ar), 132.39 (Ar), 128.12 (Ar), 127.64 (Ar), 127.50 (Ar), 126,74 (Ar), 126.60 (Ar), 126.49 (Ar), 123.11 (Ar), 119.00 (Ar), 115.7 (Ar), 113.49 (Ar), 112.67 (Ar), 92.03 (Ar), 90.91 (Ar), 69.35 (-OCH_2-), 50.47 (-CH→), 36.69, 36.62, 31.74, 31.46, 31.31, 29.57, 29.40, 29.26, 26.02, 25.36, 22.60, 22.43, 22.37, 22.30, 19.01, 18.82, 14.07, 13.96, 13.83 ppm. IR(KBr): ν = 3418, 2926, 2854, 2208 (-C≡C-), 1645, 1574, 1498, 1395, 1309, 1270, 1197, 1192, 1143, 1034, 1003, 860, 848, 820, 783, 738, 705 cm^{-1}. Anal. calcd for $C_{86}H_{96}B_2N_6O_6$: C, 77.58; H, 7.27; N, 6.31. Found: C, 76.22; H, 7.03; N, 6.21.

Poly2

Yield = 59.1% (0.11 g, 0.07 mmol). M_n = 7880. ^{1}H-NMR ($CDCl_3$): δ = 0.55 (6H, -CH_2–CH_3), 0.71 (1H), 0.87 (5H), 1.22 (8H, -CH_2-), 1.52 (4H, -CH_2-), 2.03 (4H, -CO–CH_2-), 4.75 (2H, -CH →), 6.19 (2H, -NH–CO–CH_2-), 7.29 (4H, Ar–H), 7.41 (6H, Ar–H), 7.54 (8H, Ar–H), 7.71 (1H, Ar–H), 7.79 (1H, Ar–H), 8.01 (1H, Ar–H), 8.12 (3H, Ar–H), 8.61 (2H, Ar–H), 8.79 (1H, Ar–H), 8.85 (1H, Ar–H), 8.94 (2H, Ar–H) ppm. ^{11}B-NMR ($CDCl_3$): δ = 6.35 ppm. IR (KBr): ν = 3419, 3071, 3007, 2955, 2926, 2862, 2205 (-C≡C-), 1652, 1574, 1499, 1475, 1447, 1396, 1310, 1252, 1240 (C–F), 1201 (C–F), 1144 (C–F), 1035, 1003, 882, 849, 820, 783, 711, 706 cm^{-1}. Anal. calcd for $C_{79}H_{62}B_2N_6O_4F_{20}$: C, 60.79; H, 4.00; N, 5.38. Found: C, 59.40; H, 4.07; N, 5.16.

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