Secondary Structure Modulation of Triptycene-Based One-Handed Helical Ladder Polymers through π-Extension of Achiral Segments

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Secondary Structure Modulation of Triptycene-Based One-Handed Helical Ladder Polymers through \( \pi \)-Extension of Achiral Segments

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Abstract A series of enantiopure triptycene-based one-handed helical ladder polymers containing \( \pi \)-extended achiral segments with naphthalene, fluorene, and carbazole spacers was synthesized through quantitative and chemoselective ladderization of the corresponding precursor polymers with random-coil conformations. The helical handedness (right- or left-handed) and geometry (loose coil or ribbon) of the resulting ladder polymers were readily modulated by tuning the structure of the achiral spacers despite the incorporation of the same point chirality of the triptycene unit. All the helical secondary structures are stable and robust due to the shape-persistent ladder structures, showing the characteristic and environment-independent chiroptical properties.

Key words triptycene, chirality, helical polymers, ladder formation, secondary structures, \( \pi \)-extension

Introduction Proteins and DNA are composed of L-amino acid- and D-sugar-based homochiral building blocks forming unique secondary structures, such as right-handed single- and double-stranded helices, respectively, which play a critical role in their sophisticated functions. Inspired by the biological helical systems, the precise synthesis of one-handed helical polymers and the development of their specific functionalities, related to chiral separation, asymmetric catalysis, and circularly polarized luminescence, have been extensively investigated. To date, a number of synthetic helical polymers with a controlled helical handedness have been reported but there is not much structural variation when classified by their backbone frameworks. This indicates that the diversity of the synthetic helical polymers mostly relies on the side-chain modifications and that one-handed helical polymers with novel backbone structures remain challenging synthetic targets for polymer chemists. The difficulty in constructing a stable helical structure is due to the considerable conformational freedom of the polymer backbone.

Ladder polymers are ladder-shaped macromolecules, in which the adjacent cyclic monomer units are connected by two or more chemical bonds, and their conformational freedom is highly restricted due to the ladder framework, thereby leading to the shape-persistent nature of the macromolecules. We recently reported the defect-free synthesis of a novel series of one-handed helical polymers with a rigid ladder-type backbone, namely, helical ladder polymers, through quantitative and chemoselective alkyne benzannulations of the rationally designed random-coil chiral/achiral precursor copolymers composed of alternating optically-pure (R,R)-triptycene (poly-(R,R)-A) or (R)-1,1'-spirobiindane (poly-(R)-B) and poly-(R)-C and achiral 2,5-diethyl-1-substituted \( \pi \)-phenylene segments (Figure 1a). The helical structures of the resulting helical ladder polymers, such as the helical pitch, cavity size, and handedness (right \( \alpha \)-or left \( \beta \)-handed helix), can be varied depending on the chiral units incorporated into the main chain. This ladderization approach is versatile and can be applied to the synthesis of achiral fluorene- and naphthalene-based polycyclic aromatics and graphene nanoribbons with coplanar and helical geometries.

We envisioned that structurally new helical ladders could be constructed simply by incorporating the achiral polycyclic aromatic spacers into the random-coil chiral/achiral precursor copolymers containing the same chiral segments, followed by acid-promoted intramolecular alkyne benzannulations. To this end, in this study, we designed and synthesized optically-pure 2,6-linked-triptycene-bound chiral/achiral precursor copolymers containing naphthalene-, fluorene-, and carbazole-based achiral spacers in the main chain and investigated their defect-free helical ladderization through acid-promoted alkyne benzannulations to convert three enantiomeric one-handed helical ladders with \( \pi \)-extended achiral segments (Figure 1b). The impact of the \( \pi \)-extended achiral segments incorporated into the helical ladder backbones on the helical handedness, helical geometry, and the optical and chiroptical properties, including absorption, photoluminescence (PL), optical rotation, and circular dichroism (CD), was investigated.
Results and Discussion

The naphthalene-, fluorene-, and carbazole-containing achiral \( n \)-conjugated monomers (\( \text{NA}_{\text{Bip}} \), \( \text{FL}_{\text{Bip}} \), and \( \text{CA}_{\text{Bip}} \)) with two 4-bromo-2,5-bis[2-(4-alkoxy-2,6-dimethylphenyl)ethynyl]phenyl groups were synthesized through Suzuki-Miyaura coupling of the corresponding diboronic acid esters (\( \text{NA}_{\text{Bip}} \), \( \text{FL}_{\text{Bip}} \), and \( \text{CA}_{\text{Bip}} \)) with a large excess amount (5 equiv) of 1,4-dibromobenzene derivative (\( \text{PhBBr}_2 \)) (Scheme S1). The resulting monomers were then subjected to Suzuki-Miyaura coupling copolymerizations with the optically-pure triptycene-based diboronic acid ester monomers (\( \text{R}_{\text{Tript}} \)) and (\( \text{S,S}-1 \)) to produce sequence-controlled ternary copolymers with random-coil conformations (poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-1NA, poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-1FL, and poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-1CA) as cyclization precursors (Scheme S2). The number-average molar mass \( (M_n) \) and degree of polymerization \( (DP_n) \) of the obtained copolymers were estimated to be more than \( 2.24 \times 10^4 \) and 12, respectively, by size-exclusion chromatography (SEC) (Table S1).

We then performed the helical ladderization of the random-coil precursors through acid-promoted alkyne benzannulations using trifluoroacetic acid as the acid source according to a previously reported method (Figure 2a and Scheme S3).\textsuperscript{34-36} which was completed within 7 h as confirmed by IR analysis (Figure S1).\textsuperscript{37} The \( ^1 \text{H} \) NMR spectra of the ladderization products exhibited broad, but characteristic sets of proton resonances (Figure 2b(i,iv,vi)), all of which could be unequivocally assigned by the 2D NMR analysis (Figures S3, S5, and S7). These results suggest that the intramolecular cyclizations quantitatively proceeded only at specific positions (indicated by the red circles in Figure 2a), thus leading to the formation of the one-handed helical ladder polymers without a detectable level of structural defects, poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-2NA, poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-2FL, and poly-(\( R_{\text{Tript}}-R \))- and (\( S,S \))-2CA (Figure 2a,c). The \( M_n \) values were more or less unchanged before and after the helical ladderization (Figure 2a and Scheme S3). The structural integrity of the helical ladder polymers is also supported by the fact that the alkyne benzannulations of the optically-pure 2,6-linked-triptycene-bound chiral/achiral precursor copolymers containing naphthalene-, fluorene-, and carbazole-based achiral polymeric spacer segments in the main chain.

![Figure 1](image-url)

**Figure 1** (a) Structures of one-handed helical ladder polymers (poly-(\( R_{\text{Tript}}-R \))-A, poly-(\( R_{\text{Tript}}-R \))-B, and poly-(\( R_{\text{Tript}}-R \))-C) containing optically-pure 2,6-linked-(\( R_{\text{Tript}}-R \))-triptcene and 6,6'- and 4,4'-linked-(\( R_{\text{Tript}}-R \))-1,1'-spirobifuran units, respectively. (b) Schematic illustrations of the synthesis of one-handed helical ladder polymers with \( n \)-extended achiral segments through acid-promoted intramolecular alkyne benzannulations of the optically-pure 2,6-linked-triptycene-bound chiral/achiral precursor copolymers containing naphthalene-, fluorene-, and carbazole-based achiral polymeric spacer segments in the main chain.

The possible helical ladder structures of a series of (\( R_{\text{Tript}}-R \))-triptcene-bound helical ladders, poly-(\( R_{\text{Tript}}-R \))-2NA, poly-(\( R_{\text{Tript}}-R \))-2FL, and poly-(\( R_{\text{Tript}}-R \))-2CA, with 12 repeating units optimized by molecular mechanics calculations are shown in Figure 3. Unlike the previously reported (\( R_{\text{Tript}}-R \))-triptcene-bound poly-(\( R_{\text{Tript}}-R \))-A with the (\( P \))-handed contracted tubular helical structure having a helical pitch and diameter of ca. 1.5 and 2 nm, respectively,\textsuperscript{33} poly-(\( R_{\text{Tript}}-R \))-2NA forms a (\( P \))-handed loose helical coil structure with the helical pitch and diameter of ca. 8 and 3 nm, respectively (Figure 3a), while the opposite (\( M \))-handed extended ribbon-like helices with the helical pitch of ca. 5 nm and no helical cavity are found to form for poly-(\( R_{\text{Tript}}-R \))-2FL and poly-(\( R_{\text{Tript}}-R \))-2CA (Figure 3b,c). These results indicated that the...
Figure 2 (a) Synthesis of one-handed helical ladder polymers, poly-\((R,R)\)-2NA (top), poly-\((R,R)\)-2FL (middle), and poly-\((R,R)\)-2CA (bottom), through acid-promoted alkyne benzannulations of their precursor polymers (poly-\((R,R)\)-1NA, poly-\((R,R)\)-1FL, and poly-\((R,R)\)-1CA, respectively). (b) \(^{1}H\) NMR spectra (500 MHz, CDCl\(_3\), 50 °C) of poly-\((R,R)\)-1NA (i), poly-\((R,R)\)-1FL (iii), poly-\((R,R)\)-1CA (v), and as-synthesized cyclization products (poly-\((R,R)\)-2NA (ii), poly-\((R,R)\)-2FL (iv), and poly-\((R,R)\)-2CA (vi)) obtained from poly-\((R,R)\)-1NA, poly-\((R,R)\)-1FL, and poly-\((R,R)\)-1CA, respectively. For the signal assignments and the corresponding IR spectra, see the Supporting Information, Figures S2–S7 and S1, respectively. (c) Structures of poly-\((S,S)\)-2NA, poly-\((S,S)\)-2FL, and poly-\((S,S)\)-2CA.
helical geometries as well as the helical handedness can be modulated by tuning the bond directions and cyclization positions of the achiral spacers despite the use of the single enantiomeric triptycene unit, allowing the construction of the structurally-diverse variety of both the (P)- and (M)-handed helical ladders without the design of new chiral building blocks.

The absorption spectra of the helical ladder polymers are clearly red-shifted from those of the corresponding precursor polymers (Figure 4) and poly-(R,R)-A\textsubscript{33} with the absorption edges of ca. 400 nm or less, resulting from the more planar and  

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**Figure 3** Top (i) and side (ii) views of right (P)-handed helical poly-(R,R)-2NA (a) and left (M)-handed helical poly-(R,R)-2FL (b) and poly-(R,R)-2CA (c) structures with 12 repeating units optimized by molecular mechanics (MM) calculations (Compass II force field). For simplicity, all alkoxy and alkyl pendants are replaced with methoxy and methyl groups, respectively. The structures are represented by space-filling models except for the alkoxyphenyl pendant groups, which are shown as capped-stick ones, and triptycene, achiral spacers (naphthalene, fluorene, and carbazole), and other \( \pi \)-conjugated ladder frameworks are colored in blue, pink, and yellow, respectively.

**Figure 4** Absorption, CD, and Kuhn’s disymmetry factor (\( g_{abs} \)) spectra of (R,R)- and (S,S)-triptycene-bound precursor and ladder polymers containing naphthalene- (a; poly-(R,R)-1NA (i), poly-(R,R)-2NA (ii), poly-(S,S)-1NA (iii), and poly-(S,S)-2NA (iv)), fluorene- (b; poly-(R,R)-1FL (i), poly-(R,R)-2FL (ii), poly-(S,S)-1FL (iii), and poly-(S,S)-2FL (iv)), and carbazole- (c; poly-(R,R)-1CA (i), poly-(R,R)-2CA (ii), poly-(S,S)-1CA (iii), and poly-(S,S)-2CA (iv)) based achiral units in chloroform at 25 °C. (Repeating units of polymer) = 1.0 × 10\textsuperscript{-4} M.
Due to the difference in the adopted helical handedness (showing the positive first Cotton effect) of the precursor polymers with a very weak CD (Figure 4a(ii,iv)), the observed CDs are not derived from the chiral supramolecular assemblies of the polymer chains, but from the robust one-handed helix formation. The CD patterns of poly-(R,R)-2FL and poly-(R,R)-2CA showed smaller values than those of the corresponding precursors (Figure 2a). On the other hand, all the enantiomeric pairs of the helical ladder polymers showed intense mirror-image CD signals in the corresponding main-chain absorption regions (ii and iii) in Figure 4a–c, in contrast to the precursor polymers with a very weak CD ([i and iii] in Figure 4a–c). Because the CD spectral patterns and intensities of the helical ladders were virtually independent of the polymer concentration (Figure S12), temperature (Figure S13), and solvent (Figure S14), the observed CDs are not derived from the chiral supramolecular assemblies of the polymer chains, but from the robust one-handed helix formation. The CD patterns of poly-(R,R)-2FL and poly-(R,R)-2CA with the negative first Cotton effects are roughly similar to each other (Figure 4b,c(ii)), but significantly differ from those of poly-(R,R)-2NA (Figure 4a(ii)) and poly-(R,R)-A33 showing the positive first Cotton effects, which are most likely due to the difference in the adopted helical handedness (M and P) and conformations (extended ribbon-like and loosely coiled helices) (Figure 3). Among the helical ladders, the naphthalene-embedded poly-(R,R)-2NA and (S,S)-2NA showed the most intense CD signals and its Kuhn’s dissymmetry factor ($|g_{opt}|$) reached a maximum of $> 4.6 \times 10^{-3}$ at 374 nm (Figure 4a(ii,iv)), which is almost comparable to that of poly-(R,R)-A ($|g_{opt}| = 5.0 \times 10^{-3}$)33 despite the incorporation of the additional achiral naphthalene spacers in the poly-2NA backbone.

Poly-(R,R)-2NA, poly-(R,R)-2FL, and poly-(R,R)-2CA displayed a characteristic color PL (light blue, blue, and green, respectively) depending on the $\pi$-extended achiral segments incorporated in the main chain in chloroform under irradiation at 365 nm and their absolute quantum yields ($\Phi_{\text{abs}}$) were determined to be 13, 19, and 12%, respectively (Figure 5a). As expected from the absorption properties, the nitrogen-containing poly-(R,R)-2CA showed an emission band in the longer wavelength region compared to the others (Figure 5b).41

Conclusions
In summary, we have succeeded in modulating the secondary structures of the (R,R)- and (S,S)-tritylpheine-based one-handed helical ladder polymers simply by replacing the $\pi$-extended achiral segments in the main chain while retaining the chiral monomer units. This enables the synthesis of a series of robust and shape-persistent helical ladder polymers with a different helical handedness and geometry, which contain no detectable structural defects, from the corresponding random-coil precursors containing a single enantiomer of the chiral triptycene segment through quantitative and chemoselective ladderization. We believe that the present "$\pi$-extension of the achiral segment" approach can be applied to the systematic construction of a further variety of one-handed helical ladder architectures with controllable helical handedness and geometry based on the rational design and sequence control of the chiral and achiral segments, leading to the emergence of unique properties and chiral functions characteristic of these structures.

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Supporting Information
Yes.

Primary Data
NO.

Conflict of Interest
The authors declare no conflict of interest.

References and Notes
(1) Pauling, L.; Corey, R. B.; Branson, H. R. P Natl Acad Sci USA 1951, 37, 205.
prepared by alkyne benzannulations, washed with methanol, and dried in vacuo to yield poly-(SS)-2NA as a brown solid (4.0 mg, >99% yield). [α]D^25 = -92.5 (c=0.057, CHCl₃). ^1H NMR (500 MHz, CDCl₃, 298 K): 6.93-9.12 (br, 2H, Ar-H), 9.12-8.95 (br, 2H, Ar-H), 8.95-8.75 (br, 2H, Ar-H), 8.70-8.45 (br, 2H, Ar-H), 8.35-8.10 (br, 2H, Ar-H), 8.05-7.85 (br, 2H, Ar-H), 7.75-7.60 (br, 2H, Ar-H), 7.60-7.35 (br, 4H, Ar-H), 7.10-6.95 (br, 2H, Ar-H), 6.95-6.60 (br, 8H, Ar-H), 5.85-5.65 (br, 2H, CH), 4.50-4.20 (br, 4H, CH), 2.20-1.65 (br, 40H, CH₂, CH₃), 1.65-1.20 (br, 32H, CH₂), 1.10-0.80 (br, 24H, CH₃).

The synthesis of the nitrogen-containing one-handed helical ladder polymers through the one-pot Suzuki-Miyaura coupling and Schiff’s base formation reaction has also been reported by Schneebeli and co-workers, but their detailed structural characterization has not been performed, see; Murphy, K. E.; McKay, K. T.; Schenkelberg, M.; Sharafii, M.; Vestrheim, O.; Ivanic, M.; Li, J.; Schneebeli, S. T. Angew. Chem., Int. Ed. 2022, 61, e202209772.

Fang and co-workers reported the synthesis of a carbazole-based fully n-conjugated coplanar ladder polymer through reversible ring-closing olefin metathesis, which showed the PL property similar to that of poly-2CA (Figure Sb(iii)), see; Lee, J.; Rajeeva, B. B.; Yuan, T.; Guo, Z.-H.; Lin, Y.-H.; Al-Hashimi, M.; Zheng, Y.; Fang, L. Chem. Sci. 2016, 7, 881.
Supporting Information for:

Secondary Structure Modulation of Triptycene-Based One-Handed Helical Ladder Polymers through π-Extension of Achiral Segments

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1. Instruments and Materials

**Instruments.** The melting points were measured on a Yanako melting point apparatus (Yanako, Kyoto, Japan) and were uncorrected. The NMR spectra were measured using a Varian 500AS (Agilent Technologies, Santa Clara, CA) or a Bruker Ascend 500 (Bruker Biospin, Billerica, MA) spectrometer operating at 500 MHz for $^1$H and 126 MHz for $^{13}$C using tetramethylsilane or a solvent residual peak as the internal standard. The IR spectra were recorded on a JASCO FT/IR-6X spectrophotometer (JASCO, Tokyo, Japan) equipped with a JASCO ATR PRO ONE X attenuated total reflectance (ATR) attachment (ZnSe prism). The absorption and circular dichroism (CD) spectra were obtained in a 1.0- or 10-mm quartz cell using a JASCO V-750 spectrophotometer and a JASCO J-1500 spectropolarimeter, respectively. The concentrations of the polymers were calculated based on the monomer units. The temperature was controlled with a JASCO ETCS-900 apparatus for both absorption and CD measurements. The photoluminescence (PL) spectra and fluorescence quantum yields were measured with a JASCO FP-8550 spectrofluorometer attached with a JASCO ILF-135 integrating sphere (diameter 120 mm). The size exclusion chromatography (SEC) measurements were performed with a JASCO PU-4580 liquid chromatograph equipped with a JASCO CO-4060 column oven and a JASCO MD-4015 multi-wavelength UV/VIS detector. The number-average molar mass ($M_n$) and its dispersity ($M_w/M_n$) were determined at 40 °C using a Tosoh TSKgel GMHHR-M (30 cm) SEC column (Tosoh, Tokyo, Japan), and chloroform was used as the eluent at a flow rate of 1.0 mL/min. The molar mass calibration curve was obtained with polystyrene standards (Tosoh). Recycling preparative high-performance liquid chromatography (HPLC) was performed with a JAI LC-7080 liquid chromatograph (JAI, Tokyo, Japan) equipped with a JAI UV-800LA UV detector at room temperature. JAIGEL-2HR and JAIGEL-2.5HR (60 cm × 2.0 cm (i.d.)) connected in series were used as columns (JAI), and chloroform was used as the eluent at a flow rate of 9.0 mL/min. The high-resolution mass spectra (HRMS) were recorded on a Bruker compact QTOF (Bruker Daltonics, Billerica, MA) spectrometer with atmospheric pressure chemical ionization (APCI).

**Materials.** All starting materials and anhydrous solvents were purchased from Sigma-Aldrich (St. Louis, MO), Fujifilm Wako Pure Chemical (Osaka, Japan), Tokyo Kasei (TCI, Tokyo, Japan), Nacalai Tesque, or Kanto Kagaku (Tokyo, Japan) and were used as received. 2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene ($\text{NA}_{\text{Bpin}}$)$_{\text{S1}}$, ($R,R$)- and ($S,S$)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triptycene ($\text{((R,R)}$- and ($S,S$)-1)$_{\text{S2}}$, and bis[2-(4-alkoxy-2,6-dimethylphenyl)ethynyl]phenylene compounds ($\text{PhBr}_{\text{S3}}$ and $\text{Ph}_{\text{Ph}}$)$_{\text{S4}}$) were synthesized according to the previously reported methods.
2. Synthetic Procedures

NA_{Br}, FL_{Br}, CA_{Br}, and model-2CA were prepared according to Scheme S1.

Scheme S1. Synthesis of NA_{Br}, FL_{Br}, CA_{Br}, and model-2CA.
Synthesis of NA\textsubscript{Br}. To a mixture of Ph\textsubscript{Br} (592 mg, 0.762 mmol), NA\textsubscript{Bpin} (59 mg, 0.15 mmol), and potassium carbonate (71 mg, 0.51 mmol) in a degassed toluene/water mixture (4/1, v/v; 10 mL) was added tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\textsubscript{3})\textsubscript{4}) (29 mg, 0.025 mmol). After stirring at 90 °C for 18 h, the mixture was cooled to room temperature and diluted with ethyl acetate. The solution was washed with water, and then dried over Na\textsubscript{2}SO\textsubscript{4}. The solvents were removed under reduced pressure and the residue was passed through a short pad of silica gel using n-hexane/chloroform (8/2, v/v) as the eluent. After concentrating in vacuo, the crude product was purified by recycling preparative HPLC on JAIGEL-2HR and JAIGEL-2.5HR (60 cm × 2.0 cm (i.d.)) using chloroform as the eluent to give the desired product as a yellow solid (101 mg, 43% yield). Mp: 159.8–160.5 °C. IR (ATR, cm\textsuperscript{-1}): 2200 (C≡C). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 50 °C): \textdelta 8.10 (d, J = 1.0 Hz, 2H, Ar–H), 7.92 (d, J = 8.5 Hz, 2H, Ar–H), 7.91 (s, 2H, Ar–H), 7.78 (dd, J = 8.4, 1.3 Hz, 2H, Ar–H), 7.63 (s, 2H, Ar–H), 6.61 (s, 4H, Ar–H), 6.47 (s, 4H, Ar–H), 4.25 (quint, J = 5.7 Hz, 2H, CH), 4.16 (quint, J = 5.7 Hz, 2H, CH), 2.53 (s, 12H, CH\textsubscript{3}), 1.67-1.57 (m, 16H, CH\textsubscript{2}), 1.42-1.27 (m, 32H, CH\textsubscript{2}), 0.90 (t, J = 7.0 Hz, 12H, CH\textsubscript{3}), 0.86 (t, J = 7.1 Hz, 12H, CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, rt): \textdelta 158.82, 158.64, 142.68, 142.39, 141.82, 137.39, 136.10, 133.79, 132.56, 128.09, 127.74, 127.72, 125.67, 123.54, 123.15, 114.42, 114.36, 114.20, 114.03, 94.70, 94.43, 94.01, 93.39, 77.66, 77.56, 33.65, 33.57, 27.54, 27.48, 22.79, 22.75, 21.69, 21.24, 14.07, 14.03. HRMS (APCI+): m/z calcd for C\textsubscript{98}H\textsubscript{118}Br\textsubscript{2}O\textsubscript{4} (M+), 1516.7391; found 1516.7361.

FL\textsubscript{Br} and CA\textsubscript{Br} were also prepared from 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene (FL\textsubscript{Bpin}) and 9-(9-heptadecanyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (CA\textsubscript{Bpin}) with Ph\textsubscript{Br}, respectively, in the same way for the synthesis of NA\textsubscript{Br}.

Analytical data of FL\textsubscript{Br}: Yellow solid. Yield: 51%. Mp: decomposed at > 290 °C. IR (ATR, cm\textsuperscript{-1}): 2203 (C≡C). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C): \textdelta 7.87 (s, 2H, Ar–H), 7.74 (d, J = 7.8 Hz, 2H, Ar–H), 7.63 (dd, J = 7.8, 1.5 Hz, 2H, Ar–H), 7.55 (s, 2H, Ar–H), 7.46 (d, J = 1.2 Hz, 2H, Ar–H), 6.61 (s, 4H, Ar–H), 6.48 (s, 4H, Ar–H), 4.25 (quint, J = 5.9 Hz, 2H, CH), 4.17 (quint, J = 5.9 Hz, 2H, CH), 2.53 (s, 12H, CH\textsubscript{3}), 2.17 (s, 12H, CH\textsubscript{3}), 1.92 (t, J = 8.2 Hz, 4H, CH\textsubscript{2}), 1.69-1.56 (m, 16H, CH\textsubscript{2}), 1.44-0.85 (m, 76H, CH\textsubscript{2}, CH\textsubscript{3}), 0.76 (t, J = 7.2 Hz, 10H, CH\textsubscript{2}, CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, rt): \textdelta 158.79, 158.53, 151.44, 142.89,
142.60, 142.23, 140.25, 138.57, 135.81, 133.57, 128.33, 125.50, 123.59, 123.54, 122.77, 119.27, 114.45, 114.20, 113.98, 94.77, 94.47, 93.84, 93.11, 77.66, 77.49, 55.25, 39.95, 33.64, 33.58, 31.76, 29.94, 29.23, 29.18, 27.53, 27.49, 24.02, 22.79, 22.76, 22.60, 21.61, 21.16, 14.05, 14.03. HRMS (APCI+): m/z cale(d for C$_{117}$H$_{152}$Br$_2$O$_4$ (M$^+$), 1779.0052; found 1779.0045.

Analytical data of CA$_{Br}$. Yellow solid. Yield: 30%. Mp: decomposed at > 250 °C. IR (ATR, cm$^{-1}$): 2202 (C=C). $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): δ 8.12 (dd, J = 18.5, 7.1 Hz, 2H, Ar–H), 7.88 (s, 2H, Ar–H), 7.70 (s, 1H, Ar–H), 7.63 (s, 2H, Ar–H), 7.51 (s, 1H, Ar–H), 7.48-7.45 (m, 2H, Ar–H), 6.6 (s, 4H, Ar–H), 6.43 (s, 4H, Ar–H), 4.54-4.51 (m, 1H, CH), 4.24 (quint, J = 5.8 Hz, 2H, CH), 4.13 (quint, J = 5.7 Hz, 2H, CH), 2.53 (s, 12H, CH$_3$), 2.20-2.11 (m, 2H, CH$_2$), 2.05 (s, 12H, CH$_3$), 1.90-1.84 (m, 2H, CH$_2$), 1.70-1.55 (m, 16H, CH$_2$), 1.45-1.00 (m, 56H, CH$_2$), 0.90 (t, J = 7.1 Hz, 12H, CH$_3$), 0.85 (t, J = 7.1 Hz, 12H, CH$_3$), 0.76 (t, J = 7.2 Hz, 6H, CH$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$, rt): δ 158.79, 158.51, 143.52, 142.61, 142.31, 142.22, 138.99, 137.43, 136.87, 135.61, 135.61, 133.89, 133.84, 125.38, 125.35, 123.91, 123.18, 122.74, 121.75, 121.20, 120.13, 120.01, 119.73, 114.50, 114.45, 114.20, 113.96, 112.31, 109.44, 94.87, 94.64, 93.81, 93.09, 77.66, 77.48, 56.51, 33.65, 33.55, 13.73, 29.24, 29.13, 29.10, 27.54, 27.47, 26.78, 22.79, 22.76, 22.60, 21.62, 20.91, 14.06, 14.02. HRMS (APCI+): m/z cale(d for C$_{117}$H$_{152}$Br$_2$NO$_4$ (M$^+$), 1794.0161; found 1794.0162.

**Synthesis of model-ICA.** To a mixture of Ph$_{Ph}$ (50 mg, 0.079 mmol), CA$_{Bpin}$ (24 mg, 0.036 mmol), and tripotassium phosphate (46 mg, 0.22 mmol) in a degassed tetrahydrofuran (THF)/water mixture (2/1, v/v; 0.90 mL) was added chloro[(tri-tert-butylphosphine)-2-(2-aminobiphenyl)]palladium(II) (P(t-Bu)$_2$) (2.4 mg, 4.7 μmol). After stirring at 60 °C for 16 h, the mixture was diluted with chloroform and the solution was washed with water, and then dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was passed through a short pad of silica gel using n-hexane/chloroform (6/4, v/v) as the eluent. After concentrating in vacuo, the crude product was purified by recycling preparative HPLC on JAIHEL-2HR and JAIHEL-2.5HR (60 cm × 2.0 cm (i.d.)) using chloroform as the eluent to give the desired product as a colorless oil (26 mg, 47% yield). Mp: 179.3–180.1 °C. IR (ATR, cm$^{-1}$): 2201 (C=C). $^1$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 90 °C): δ 8.20 (d, J = 8.2 Hz, 2H, Ar–H), 7.81-7.74 (m, 10H, Ar–H), 7.63 (d, J = 7.9 Hz, 2H, Ar–H), 7.51 (m, 4H, Ar–H), 7.44 (t, J = 7.2 Hz, 2H, Ar–H), 6.60 (s, 4H, Ar–H), 6.53 (s, 4H, Ar–H), 4.67-4.57 (br, 1H, NCH),
3.99 (t, J = 6.4 Hz, 4H, OCH$_2$), 3.93 (t, J = 6.6 Hz, 4H, OCH$_2$), 2.31 (s, 12H, CH$_3$), 2.31-2.23 (m, 2H, CH$_2$), 2.17 (s, 12H, CH$_3$), 2.02-1.96 (m, 2H, CH$_2$), 1.81-1.72 (m, 8H, CH$_2$), 1.56-1.45 (m, 8H, CH$_2$), 1.23-1.10 (m, 24H, CH$_2$), 1.03-0.98 (m, 12H, CH$_3$), 0.83 (t, J = 7.2 Hz, 6H, CH$_3$).

$^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 90 °C): δ 158.82, 158.75, 143.31, 142.07, 141.91, 141.61, 140.17, 137.65, 133.94, 133.32, 129.12, 127.98, 127.34, 122.69, 122.06, 120.34, 119.53, 115.22, 113.25, 113.13, 95.98, 95.92, 92.04, 67.67, 67.58, 56.65, 33.73, 31.47, 31.19, 29.06, 28.84, 26.81, 22.29, 20.90, 20.69, 19.02, 19.00, 13.69, 13.52, 13.50.

HRMS (APCI+): m/z calc'd for C$_{109}$H$_{124}$NO$_4$ (M+H$^+$), 1510.9525; found 1510.9526.

**Synthesis of model-2CA.** Model-1CA (7.2 mg, 4.8 µmol) was dissolved in an anhydrous dichloromethane/trifluoroacetic acid (TFA) mixture (50/1, v/v; 2.0 mL) and the solution was stirred at room temperature for 1 h. After quenching the reaction with saturated aqueous NaHCO$_3$, the mixture was diluted with chloroform and the solution was washed with saturated aqueous NaHCO$_3$ and water, and then dried over Na$_2$SO$_4$. The solvents were removed under reduced pressure and the product was passed through a short pad of silica gel using chloroform as the eluent to give the desired product as a yellow solid (7.1 mg, 99% yield). Mp: > 300 °C. $^1$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 90 °C): δ 9.29 (s, 2H, Ar–H), 9.21 (s, 2H, Ar–H), 9.02-8.97 (m, 4H, Ar–H), 8.15 (s, 2H, Ar–H), 7.95 (s, 2H, Ar–H), 7.75 (t, J = 7.0 Hz, 2H, Ar–H), 7.72 (s, 2H, Ar–H), 7.59-7.54 (m, 4H, Ar–H), 6.87 (s, 8H, Ar–H), 5.15-5.05 (br, 1H, NCH), 4.18 (t, J = 6.6 Hz, 4H, OCH$_2$), 4.15 (t, J = 6.4 Hz, 4H, OCH$_2$), 2.75-2.67 (m, 2H, CH$_2$), 2.40-2.34 (m, 2H, CH$_2$), 2.13 (s, 12H, CH$_3$), 2.11 (s, 12H, CH$_3$), 2.00-1.88 (m, 8H, CH$_2$), 1.74-1.60 (m, 8H, CH$_2$), 1.58-1.10 (m, 36H), 0.72 (t, J = 6.3 Hz, 6H). $^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 90 °C): δ 158.43, 158.37, 138.21, 137.20, 132.32, 131.87, 131.00, 130.41, 130.32, 129.80, 129.29, 128.88, 128.05, 126.92, 126.46, 126.17, 125.47, 125.37, 122.96, 121.64, 121.57, 118.05, 113.74, 67.88, 67.79, 57.07, 33.79, 31.59, 31.48, 31.40, 29.44, 29.31, 29.11, 28.85, 27.06, 22.17, 20.58, 20.41, 19.26, 19.20, 13.76, 13.67, 13.55. HRMS (APCI+): m/z calc'd for C$_{109}$H$_{124}$NO$_4$ (M+H$^+$), 1510.9525; found 1510.9524.
**Polymerization.** Poly-(R,R)-1NA, poly-(S,S)-1NA, poly-(R,R)-1FL, poly-(S,S)-1FL, poly-(R,R)-1CA, and poly-(S,S)-1CA were prepared by Suzuki–Miyaura coupling copolymerizations of NA\(_{Br}\), FL\(_{Br}\), and CA\(_{Br}\) with (R,R)- and (S,S)-1 in a dry Schlenk flask under a dry nitrogen atmosphere (Scheme S2). The results of the copolymerizations are summarized in Table S1. A typical procedure for the copolymerization of NA\(_{Br}\) with (R,R)-1 is described as follows.

NA\(_{Br}\) (50 mg, 0.033 mmol), (R,R)-1 (17 mg, 0.033 mmol), and tripotassium phosphate (51 mg, 0.24 mmol) were placed in a dry Schlenk flask, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a degassed THF/water mixture (2/1, v/v; 1.5 mL) was added using a syringe. To this was added P(t-Bu)_3 Pd G2 (8.0 mg, 0.016 mmol) and the mixture was stirred at room temperature for 20 h, and then diluted with chloroform. The solution was washed with water, and then dried over Na\(_2\)SO\(_4\). After filtration, most of the solvent was removed under reduced pressure. The resulting polymer was then precipitated into a large amount of methanol, collected by centrifugation, washed with n-hexane, and dried in vacuo at room temperature (42 mg, 80% yield) (entry 1 in Table S1). In the same way, poly-(S,S)-1NA, poly-(R,R)-1FL, poly-(S,S)-1FL, poly-(R,R)-1CA, and poly-(S,S)-1CA were prepared (entries 2–6). The \(M_n\) and \(M_w/M_n\) values of the polymers were estimated by SEC using polystyrene standards in chloroform.
Table S1 Copolymerization results of NABr, FLBr, and CABr with (R,R)- and (S,S)-1 using P(t-Bu)3Pd G2 in the presence of K3PO4 in THF/H2O (2/1, v/v) at room temperature for 20 h

<table>
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<tr>
<th>Entry</th>
<th>Monomer in feed (mol%)</th>
<th>Copolymer Sample code</th>
<th>Yield (%)</th>
<th>$M_n (10^4)$b</th>
<th>$M_w/M_n$ b</th>
<th>DPn c</th>
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<td>1</td>
<td>NABr (50) (R,R)-1 (50)</td>
<td>poly-(R,R)-1NA</td>
<td>80</td>
<td>2.71</td>
<td>1.85</td>
<td>17</td>
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<tr>
<td>2</td>
<td>NABr (50) (S,S)-1 (50)</td>
<td>poly-(S,S)-1NA</td>
<td>26</td>
<td>2.85</td>
<td>3.30</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>FLBr (50) (R,R)-1 (50)</td>
<td>poly-(R,R)-1FL</td>
<td>30</td>
<td>2.24</td>
<td>1.98</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>FLBr (50) (S,S)-1 (50)</td>
<td>poly-(S,S)-1FL</td>
<td>36</td>
<td>3.83</td>
<td>4.62</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>CABr (50) (R,R)-1 (50)</td>
<td>poly-(R,R)-1CA</td>
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<td>3.28</td>
<td>2.16</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>CABr (50) (S,S)-1 (50)</td>
<td>poly-(S,S)-1CA</td>
<td>54</td>
<td>6.92</td>
<td>4.89</td>
<td>37</td>
</tr>
</tbody>
</table>

a $[1] = 33$ mM, [P(t-Bu)3Pd G2] = 16 mM, [P(t-Bu)3Pd G2]/[K3PO4] = 1/15. b Estimated by SEC (polystyrene standards) with chloroform as the eluent. c Number-average degree of polymerization estimated by $M_n$.

Analytical data of poly-(R,R)-1NA: Pale yellow solid. $[\alpha]_{D}^{25} +154.6$ (c 0.34, CHCl3). IR (ATR, cm⁻¹): 2199 (C≡C). 1H NMR (500 MHz, CDCl3, 50 °C): δ 8.17 (s, 2H, Ar–H), 7.95 (d, $J = 8.9$ Hz, 2H, Ar–H), 7.86 (d, $J = 8.5$ Hz, 2H, Ar–H), 7.78 (s, 2H, Ar–H), 7.72 (s, 2H, Ar–H), 7.64 (s, 2H, Ar–H), 7.46 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.39 (d, $J = 3.7$ Hz, 2H, Ar–H), 7.28 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.04 (t, $J = 3.7$ Hz, 2H, Ar–H), 6.45 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.52 (s, 2H, CH), 4.17-4.13 (m, 4H, CH), 2.19-1.87 (m, 24H, CH3), 1.61-1.52 (m, 16H, CH2), 1.39-1.25 (m, 32H, CH2), 0.88-0.84 (m, 24H, CH3).
Analytical data of poly-(S,S)-1NA: Pale yellow solid. [α]^{25}_D –155.3 (c 0.31, CHCl₃). IR (ATR, cm⁻¹): 2200 (C≡C). ¹H NMR (500 MHz, CDCl₃, 50 °C): δ 8.17 (s, 2H, Ar–H), 7.95 (d, J = 8.8 Hz, 2H, Ar–H), 7.86 (d, J = 8.3 Hz, 2H, Ar–H), 7.78 (s, 2H, Ar–H), 7.72 (s, 2H, Ar–H), 7.64 (s, 2H, Ar–H), 7.46 (d, J = 7.6 Hz, 2H, Ar–H), 7.39 (d, J = 3.2 Hz, 2H, Ar–H), 7.28 (d, J = 7.8 Hz, 2H, Ar–H), 7.04 (t, J = 3.7 Hz, 2H, Ar–H), 6.45 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.52 (s, 2H, CH), 4.18–4.12 (m, 4H, CH), 2.19–1.87 (m, 24H, CH₃), 1.60–1.52 (m, 16H, CH₂), 1.39–1.27 (m, 32H, CH₂), 0.88–0.84 (m, 24H, CH₃).

Analytical data of poly-(R,R)-1FL: Pale yellow solid. [α]^{25}_D +95.1 (c 0.32, CHCl₃). IR (ATR, cm⁻¹): 2201 (C≡C). ¹H NMR (500 MHz, CDCl₃, 50 °C): δ 7.76–7.71 (m, 6H, Ar–H), 7.63 (s, 2H, Ar–H), 7.60 (s, 2H, Ar–H), 7.53 (s, 2H, Ar–H), 7.44 (d, J = 7.6 Hz, 2H, Ar–H), 7.41–7.35 (br, 2H, Ar–H), 7.30–7.25 (br, 2H, Ar–H), 7.05–6.95 (br, 2H, Ar–H), 6.47 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.51 (s, 2H, CH), 4.20–4.10 (br, 4H, CH), 2.17 (s, 12H, CH₃), 2.05–1.80 (br, 16H, CH₂, CH₃), 1.70–1.50 (br, 16H, CH₂), 1.45–1.20 (br, 32H, CH₂), 1.20–0.70 (br, 54H, CH₂, CH₃).

Analytical data of poly-(S,S)-1FL: Pale yellow solid. [α]^{25}_D –95.5 (c 0.32, CHCl₃). IR (ATR, cm⁻¹): 2201 (C≡C). ¹H NMR (500 MHz, CDCl₃, 50 °C): δ 7.76–7.69 (m, 6H, Ar–H), 7.63 (s, 2H, Ar–H), 7.60 (s, 2H, Ar–H), 7.53 (s, 2H, Ar–H), 7.44 (d, J = 7.6 Hz, 2H, Ar–H), 7.41–7.33 (br, 2H, Ar–H), 7.30–7.25 (br, 2H, Ar–H), 7.06–6.95 (br, 2H, Ar–H), 6.47 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.51 (s, 2H, CH), 4.20–4.10 (br, 4H, CH), 2.17 (s, 12H, CH₃), 2.05–1.80 (br, 16H, CH₂, CH₃), 1.70–1.50 (br, 16H, CH₂), 1.45–1.20 (br, 32H, CH₂), 1.20–0.70 (br, 54H, CH₂, CH₃).
Analytical data of poly-(R,R)-1CA: Pale yellow solid. [α]^{25}_D +138.4 (c 0.31, CHCl₃). IR (ATR, cm⁻¹): 2201 (C≡C). "H NMR (500 MHz, CDCl₃, 50 °C): δ 8.25-8.15 (br, 2H, Ar–H), 7.78 (s, 2H, Ar–H), 7.71 (s, 2H, Ar–H), 7.62 (s, 2H, Ar–H), 7.60-7.50 (br, 4H, Ar–H), 7.45 (d, J = 7.6 Hz, 2H, Ar–H), 7.43-7.35 (br, 2H, Ar–H), 7.29 (d, J = 7.3 Hz, 2H, Ar–H), 7.10-7.00 (br, 2H, Ar–H), 6.42 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.52 (s, 2H, CH), 4.65-4.45 (s, 1H, CH), 4.17-4.10 (m, 4H, CH), 2.21-1.87 (m, 28H, CH₂, CH₃), 1.64-1.53 (m, 16H, CH₂), 1.39-1.04 (m, 56H, CH₂), 0.88-0.75 (m, 30H, CH₃).

Analytical data of poly-(S,S)-1CA: Pale yellow solid. [α]^{25}_D −139.0 (c 0.29, CHCl₃). IR (ATR, cm⁻¹): 2201 (C≡C). "H NMR (500 MHz, CDCl₃, 50 °C): δ 8.25-8.15 (br, 2H, Ar–H), 7.78 (s, 2H, Ar–H), 7.71 (s, 2H, Ar–H), 7.62 (s, 2H, Ar–H), 7.60-7.50 (br, 4H, Ar–H), 7.45 (d, J = 7.6 Hz, 2H, Ar–H), 7.41-7.34 (br, 2H, Ar–H), 7.29 (d, J = 7.0 Hz, 2H, Ar–H), 7.10-7.00 (br, 2H, Ar–H), 6.42 (s, 4H, Ar–H), 6.41 (s, 4H, Ar–H), 5.52 (s, 2H, CH), 4.65-4.45 (s, 1H, CH), 4.17-4.09 (m, 4H, CH), 2.21-1.87 (m, 28H, CH₂, CH₃), 1.64-1.53 (m, 16H, CH₂), 1.39-1.03 (m, 56H, CH₂), 0.88-0.75 (m, 30H, CH₃).
Alkyne Benzannulation of Precursor Polymers. Poly-(R,R)-2NA, poly-(S,S)-2NA, poly-(R,R)-2FL, poly-(S,S)-2FL, poly-(R,R)-2CA, and poly-(S,S)-2CA were prepared by alkyne benzannulations of the corresponding precursor polymers (poly-(R,R)-1NA, poly-(S,S)-1NA, poly-(R,R)-1FL, poly-(S,S)-1FL, poly-(R,R)-1CA, and poly-(S,S)-1CA, respectively) with TFA in a dry Schlenk flask under a dry nitrogen atmosphere (Scheme S3 and Figure 2a). A typical procedure for the alkyne benzannulation of poly-(S,S)-2NA is described as follows.

The precursor polymer poly-(S,S)-1NA (4.0 mg, 2.5 µmol) was placed in a dry Schlenk flask, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, an anhydrous dichloromethane/TFA mixture (50/1, v/v; 2.0 mL) was added using a syringe. After stirring at room temperature for 3 h, the reaction mixture was diluted with ethyl acetate and the solution was washed with saturated aqueous NaHCO₃ and water, and then dried over Na₂SO₄. After filtration, most of the solvents were removed under reduced pressure and the concentrated solution was poured into a large amount of methanol. The resulting polymer was collected by centrifugation, washed with methanol, and dried in vacuo to yield poly-(S,S)-2NA as a brown solid (4.0 mg, >99% yield). In the same way, the alkyne benzannulation of poly-(R,R)-1NA, poly-(R,R)-1FL, poly-(S,S)-1FL, poly-(R,R)-1CA, and poly-(S,S)-1CA was carried out to prepare poly-(R,R)-2NA, poly-(R,R)-2FL, poly-(S,S)-2FL, poly-(R,R)-2CA, and poly-(S,S)-2CA, respectively. The $M_n$ and $M_w/M_n$ values of the helical ladder polymers were estimated by SEC using polystyrene standards in chloroform.
(Scheme S3 to be continued)

Analytical data of poly-(R,R)-2NA: Brown solid. Yield: 98%. \([\alpha]_{D}^{25} +138.4\)

\[ M_n: 3.28 \times 10^4 \]

\[ M_n/M_n: 2.16 \]

1H NMR (500 MHz, CDCl3, 50 °C): δ9.30-9.12 (br, 2H, Ar=H), 9.12-9.00 (br, 2H, Ar=H), 9.00-8.80 (br, 2H, Ar=H), 8.70-8.45 (br, 2H, Ar=H), 8.35-8.10 (br, 2H, Ar=H), 8.05-7.80 (br, 2H, Ar=H), 7.75-7.60 (br, 2H, Ar=H), 7.60-7.30 (br, 4H, Ar=H), 7.10-6.95 (br, 2H, Ar=H), 6.95-6.60 (br, 8H, Ar=H), 5.85-5.60 (br, 2H, CH), 4.55-4.20 (br, 4H, CH), 2.20-1.65 (br, 40H, CH2, CH3), 1.65-1.20 (br, 32H, CH2), 1.10-0.80 (br, 24H, CH3).
Analytical data of poly-(S,S)-2NA: Brown solid. Yield: >99%. [α]$_{D}^{25}$ = -923.5 (c 0.057, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): δ 9.30-9.12 (br, 2H, Ar–H), 9.12-8.95 (br, 2H, Ar–H), 8.95-8.75 (br, 2H, Ar–H), 8.70-8.45 (br, 2H, Ar–H), 8.35-8.10 (br, 2H, Ar–H), 8.05-7.85 (br, 2H, Ar–H), 7.75-7.60 (br, 2H, Ar–H), 7.60-7.35 (br, 4H, Ar–H), 7.10-6.95 (br, 2H, Ar–H), 6.95-6.60 (br, 8H, Ar–H), 5.85-5.65 (br, 2H, CH), 4.50-4.20 (br, 4H, CH), 2.20-1.65 (br, 40H, CH$_2$, CH$_3$), 1.65-1.20 (br, 32H, CH$_3$), 1.10-0.80 (br, 24H, CH$_3$).

Analytical data of poly-(R,R)-2FL: Pale yellow solid. Yield: >99%. [α]$_{D}^{25}$ = +64.0 (c 0.072, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): δ 9.30-8.95 (br, 4H, Ar–H), 8.95-8.60 (br, 4H, Ar–H), 7.90-7.30 (br, 10H, Ar–H), 7.10-6.90 (br, 2H, Ar–H), 6.85-6.60 (br, 8H, Ar–H), 5.80-5.65 (br, 2H, CH), 4.50-4.10 (br, 4H, CH), 2.40-1.65 (br, 44H, CH$_3$, CH$_2$), 1.65-0.45 (br, 86H, CH$_3$, CH$_2$).

Analytical data of poly-(S,S)-2FL: Pale yellow solid. Yield: >99%. [α]$_{D}^{25}$ = -66.7 (c 0.10, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): δ 9.30-9.00 (br, 4H, Ar–H), 9.00-8.60 (br, 4H, Ar–H), 7.90-7.35 (br, 10H, Ar–H), 7.10-6.90 (br, 2H, Ar–H), 6.85-6.60 (br, 8H, Ar–H), 5.85-5.65 (br, 2H, CH), 4.50-4.15 (br, 4H, CH), 2.40-1.65 (br, 44H, CH$_3$, CH$_2$), 1.65-0.45 (br, 86H, CH$_3$, CH$_2$).
Analytical data of poly-(R,R)-2CA: Brown solid. Yield: >99%. \([\alpha]^{25}_D +27.2\ (c\ 0.12,\ \text{CHCl}_3)\). \(^1\)H NMR (500 MHz, CDCl\(_3\), 50 °C): \(\delta\ 9.40-8.50\ (\text{br},\ 6\text{H},\ \text{Ar–H}),\ 8.30-7.90\ (\text{br},\ 2\text{H},\ \text{Ar–H}),\ 7.90-7.30\ (\text{br},\ 10\text{H},\ \text{Ar–H}),\ 7.10-6.90\ (\text{br},\ 2\text{H},\ \text{Ar–H}),\ 6.90-6.55\ (\text{br},\ 8\text{H},\ \text{Ar–H}),\ 5.95-5.50\ (\text{br},\ 2\text{H},\ \text{CH}),\ 5.10-4.80\ (\text{br},\ 1\text{H},\ \text{CH}),\ 4.50-4.10\ (\text{br},\ 4\text{H},\ \text{CH}),\ 2.40-1.65\ (\text{br},\ 44\text{H},\ \text{CH}_2,\ \text{CH}_3),\ 1.65-0.80\ (\text{br},\ 80\text{H},\ \text{CH}_2),\ 0.80-0.50\ (\text{br},\ 6\text{H},\ \text{CH}_3).

Analytical data of poly-(S,S)-2CA: Brown solid. Yield: >99%. \([\alpha]^{25}_D -28.5\ (c\ 0.098,\ \text{CHCl}_3)\). \(^1\)H NMR (500 MHz, CDCl\(_3\), 50 °C): \(\delta\ 9.40-8.60\ (\text{br},\ 6\text{H},\ \text{Ar–H}),\ 8.30-7.95\ (\text{br},\ 2\text{H},\ \text{Ar–H}),\ 7.90-7.30\ (\text{br},\ 10\text{H},\ \text{Ar–H}),\ 7.10-6.90\ (\text{br},\ 2\text{H},\ \text{Ar–H}),\ 6.90-6.60\ (\text{br},\ 8\text{H},\ \text{Ar–H}),\ 5.90-5.50\ (\text{br},\ 2\text{H},\ \text{CH}),\ 5.10-4.80\ (\text{br},\ 1\text{H},\ \text{CH}),\ 4.50-4.10\ (\text{br},\ 4\text{H},\ \text{CH}),\ 2.40-1.65\ (\text{br},\ 44\text{H},\ \text{CH}_2,\ \text{CH}_3),\ 1.65-0.80\ (\text{br},\ 80\text{H},\ \text{CH}_2),\ 0.80-0.50\ (\text{br},\ 6\text{H},\ \text{CH}_3).

The molecular modeling and molecular mechanics (MM) calculations were conducted using the Compass II force field\textsuperscript{85} as implemented in the Materials Studio Modeling software (Version 8.0; Dassault Systèmes BIOVIA, San Diego, CA, USA) operated using a PC running under Windows 10. The polymer models of a right (P)-handed helical poly-(R,R)-2NA and left (M)-handed helical poly-(R,R)-2FL and poly-(R,R)-2CA (12 repeating monomer units), in which the branched alkoxy and the branched/long alkyl groups were replaced by the methoxy and methyl groups, respectively, for simplicity, were constructed (poly-(R,R)-2NA-OMe, poly-(R,R)-2FL-OMe, and poly-(R,R)-2CA-OMe) by a Polymer Builder module in the Materials Studio Modeling software according to the following procedures: first, the initial structures of the unimer model compounds ((R,R)-2NA-OMe, (R,R)-2FL-OMe, and (R,R)-2CA-OMe) were constructed on a Windows 10 PC with the GaussView 6 (Gaussian, Inc., Pittsburgh, PA). The structures were fully optimized by the density functional theory (DFT) calculations using the B3LYP\textsuperscript{6-7} functional with the 6-31G(d) basis set\textsuperscript{8-10} in Gaussian 16 software.\textsuperscript{51} The polymer backbones were constructed based on the bond lengths, bond angles, and internal rotation angles of the optimized structures of the corresponding unimer models. The end groups of poly-(R,R)-2NA-OMe, poly-(R,R)-2FL-OMe, and poly-(R,R)-2CA-OMe were then added to the polymer backbones. The dielectric constant was set to 1.0. The calculation was used with setup parameters that include a 0.001 kcal/mol/Å final convergence for minimization. The whole structures were then geometry-optimized with a cutoff distance of 18.5 Å by the conjugate gradient method. Computer resources for the DFT calculations were provided by the Information Technology Center of Nagoya University.
4. Supporting Data

Figure S1. IR spectra of poly-(R,R)-1NA (a), poly-(S,S)-1NA (c), poly-(R,R)-1FL (e), poly-(S,S)-1FL (g), poly-(R,R)-1CA (i), poly-(S,S)-1CA (k), and those of the as-synthesized products after acid-promoted cyclizations in a dichloromethane/TFA (50/1, v/v) mixture at room temperature, measured in ATR mode at room temperature.
Figure S2. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, CDCl₃, 50 °C, mixing time = 500 ms (NOESY)) of poly-(S,S)-1NA.
Figure S3. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, CDCl₃, 50 °C, mixing time = 500 ms (NOESY)) of poly-(S,S)-2NA.
Figure S4. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, CDCl₃, 50 °C, mixing time = 500 ms (NOESY)) of poly-(R,R)-1FL.
Figure S5. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, CDCl$_3$, 50 °C, mixing time = 500 ms (NOESY)) of poly-(R,R)-2FL.
Figure S6. Partial COSY (a,b) and NOESY (c,d) spectra (500 MHz, CDCl₃, 50 °C, mixing time = 500 ms (NOESY)) of poly-(S,S)-1CA.
Figure S7. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, CDCl$_3$, 50 °C, mixing time = 500 ms (NOESY)) of poly-(S,S)-2CA.
Figure S8. Quantitative and chemoselective synthesis of ladder-type molecules ((R,R)-model-2TR (a), model-2NA (b), and model-2FL (c)) through acid-promoted alkyne benzannulations of (R,R)-model-1TR, model-1NA, and model-1FL, respectively. The data are cited from refs. S12 and S13.
Figure S9. (a) $^1$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C) and (b) IR (ATR, rt) spectra of model-1CA (i) and those of the as-synthesized product (model-2CA) (ii) after acid-promoted cyclizations in a dichloromethane/TFA (50/1, v/v) mixture at rt for 1 h. For the signal assignments of (a), see Figures S10 and S11.
Figure S10. Partial COSY (a) and ROESY (b,c) spectra (500 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C, mixing time = 500 ms (ROESY)) of model-1CA.
Figure S11. Partial COSY (a) and NOESY (b,c) spectra (500 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C, mixing time = 500 ms (NOESY)) of model-2CA.
**Figure S12.** CD and absorption spectra of poly-(R,R)-2NA (a), poly-(R,R)-2FL (b), and poly-(R,R)-2CA (c) in chloroform at 25 °C before (i and ii) and after filtration of (i) through a membrane filter with a pore size of 0.22 µm (iii). The spectra were measured in 1.0- (0.10 mM (i) and (iii)) and 10-nm (0.010 (ii) mM) cells.
Figure S13. CD and absorption spectra of poly-(R,R)-2NA (a), poly-(R,R)-2FL (b), and poly-(R,R)-2CA (c) in 1,1,2,2-tetrachloroethane at different temperatures (–10 (i), 25 (ii), 50 (iii), and 80 (iv) °C). [Repeating units of polymer] = 1.0 × 10^{-4} M.
Figure S14. CD and absorption spectra of poly-\((R,R)\)-2NA (a), poly-\((R,R)\)-2FL (b), and poly-\((R,R)\)-2CA (c) in different solvents (toluene (i), chloroform (ii), 1,1,2,2-tetrachloroethane (iii), and THF (iv)) at 25 °C. [Repeating units of polymer] = 1.0 \times 10^{-4} \text{ M}. 
5. Supporting References


6. $^1$H and $^{13}$C NMR Spectral Data

![Figure S15. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of NA$_{Br}$.](image1)

![Figure S16. $^{13}$C NMR (126 MHz, CDCl$_3$, rt) spectrum of NA$_{Br}$.](image2)
Figure S17. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C) spectrum of FL$_{Br}$.

Figure S18. $^{13}$C NMR (126 MHz, CDCl$_3$, rt) spectrum of FL$_{Br}$.
Figure S19. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C) spectrum of CA$_{Br}$.

Figure S20. $^{13}$C NMR (126 MHz, CDCl$_3$, rt) spectrum of CA$_{Br}$.
Figure S21. $^1$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C) spectrum of model-1CA.

Figure S22. $^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C) spectrum of model-1CA.
**Figure S23.** $^1$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C) spectrum of model-2CA.

**Figure S24.** $^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-$d_2$, 90 °C) spectrum of model-2CA.
Figure S25. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-(R,R)-1NA.

Figure S26. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-(S,S)-1NA.
**Figure S27.** $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-($R$,$R$)-1FL.

**Figure S28.** $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-($S$,$S$)-1FL.
**Figure S29.** $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-(R,R)-1CA.

**Figure S30.** $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-(S,S)-1CA.
Figure S31. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-$(R,R)$-2NA.

Figure S32. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-$(S,S)$-2NA.
Figure S33. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-$(R,R)$-2FL.

Figure S34. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-$(S,S)$-2FL.
Figure S35. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-($R,R$)-2CA.

Figure S36. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C) spectrum of poly-($S,S$)-2CA.