

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

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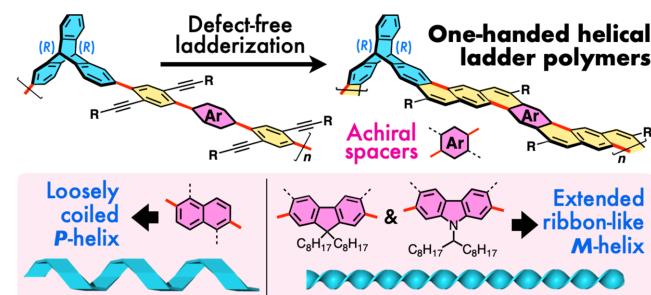
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Abstract A series of enantiopure triptycene-based one-handed helical ladder polymers containing π -extended achiral segments with naphthalene, fluorene, and carbazole spacers was synthesized through quantitative and chemoselective ladderization of 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: alkyne benzannulations, chirality, helical polymers, ladder formation, secondary structures, π -extension

Introduction

Proteins¹ and DNA² composed of L-amino acid- and D-sugar-based homochiral building blocks form unique secondary structures, such as right-handed single- and double-stranded helices, respectively, which play a critical role in their sophisticated functions.³ Inspired by the biological helical systems, the precise synthesis of one-handed helical polymers^{4–13} and the development of their specific functionalities, related to chiral separation,^{14–17} asymmetric catalysis,^{18–21} and circularly polarized luminescence,²² have been extensively investigated. To date, a number of synthetic helical polymers with a controlled helical handedness have been reported,^{5,6,9} 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.^{23–30} 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^{31,32} of the rationally designed random-coil chiral/achiral precursor copolymers composed of alternating optically pure (R,R)-triptycene (poly-(R,R)-A)³³ or (R)-1,1'-spirobiindane (poly-(R)-B³⁴ and poly-(R)-C³⁵) and achiral 2,5-diethynyl-substituted p-phenylene segments (Figure 1a). The helical structures of the resulting helical ladder polymers, such as the helical pitch, cavity size, and handedness (right (P)- or left (M)-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 aromatics³⁵ and graphene nanoribbons with coplanar³⁵ and helical³⁶ 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/

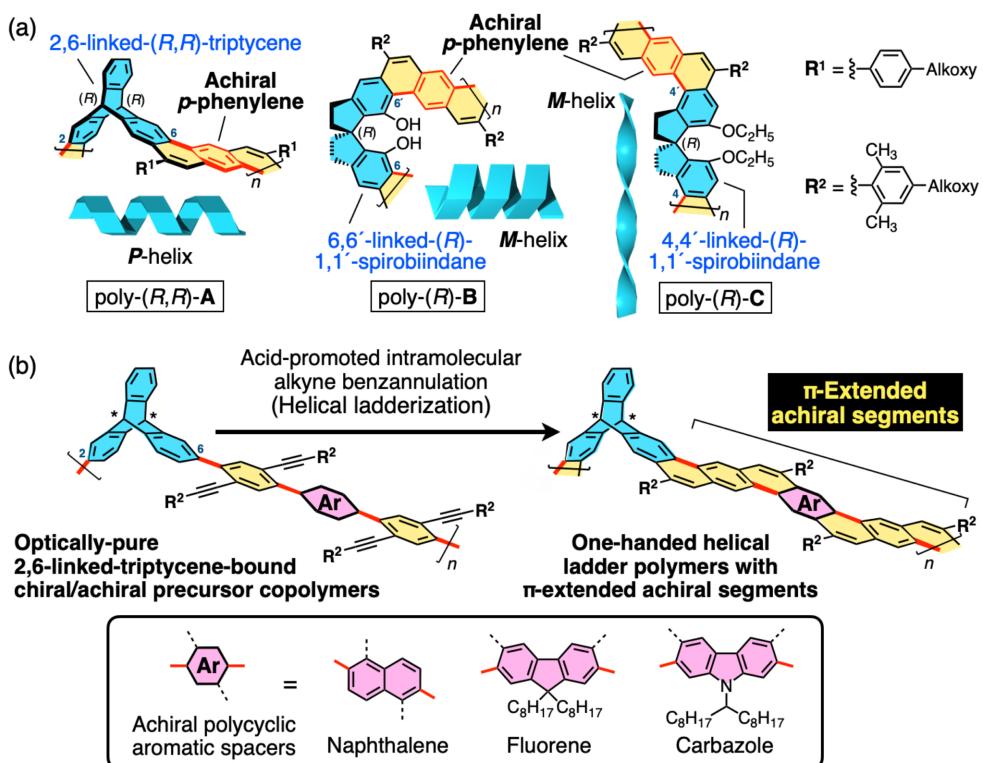


Figure 1 (a) Structures of one-handed helical ladder polymers (poly-(R,R)-A, poly-(R)-B, and poly-(R)-C) containing optically pure 2,6-linked-(R,R)-trptycene and 6,6'- and 4,4'-linked-(R)-1,1'-spirobiindane units, respectively. (b) Schematic illustrations of the synthesis of one-handed helical ladder polymers with π -extended achiral segments through acid-promoted intramolecular alkyne benzannulations of the optically pure 2,6-linked-trptycene-bound chiral/achiral precursor copolymers containing naphthalene-, fluorene-, and carbazole-based achiral polycyclic aromatic spacers in the main chain.

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 π -extended achiral segments (Figure 1b). The impact of the π -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 π -conjugated monomers (**NA_{Br}**, **FL_{Br}**, and **CA_{Br}**) 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 (**NA_{Bpin}**, **FL_{Bpin}**, and **CA_{Bpin}**, respectively) with a large excess amount (5 equiv) of the 1,4-dibromobenzene derivative (**Ph_{Br}**)

(Scheme S1). The resulting monomers were then subjected to Suzuki–Miyaura coupling copolymerizations with the optically pure triptycene-based diboronic acid ester monomers ((R,R)- and (S,S)-**1**) to produce sequence-controlled ternary copolymers with random-coil conformations (poly-(R,R)- and (S,S)-**1NA**, poly-(R,R)- and (S,S)-**1FL**, and poly-(R,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 2.24×10^4 and 12, respectively, by size-exclusion chromatography (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),^{34–36} which was completed within 7 h as confirmed by IR analysis (Figure S1).³⁷ The ¹H NMR spectra of the ladderization products exhibited broad, but characteristic sets of proton resonances (Figure 2b (ii, 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

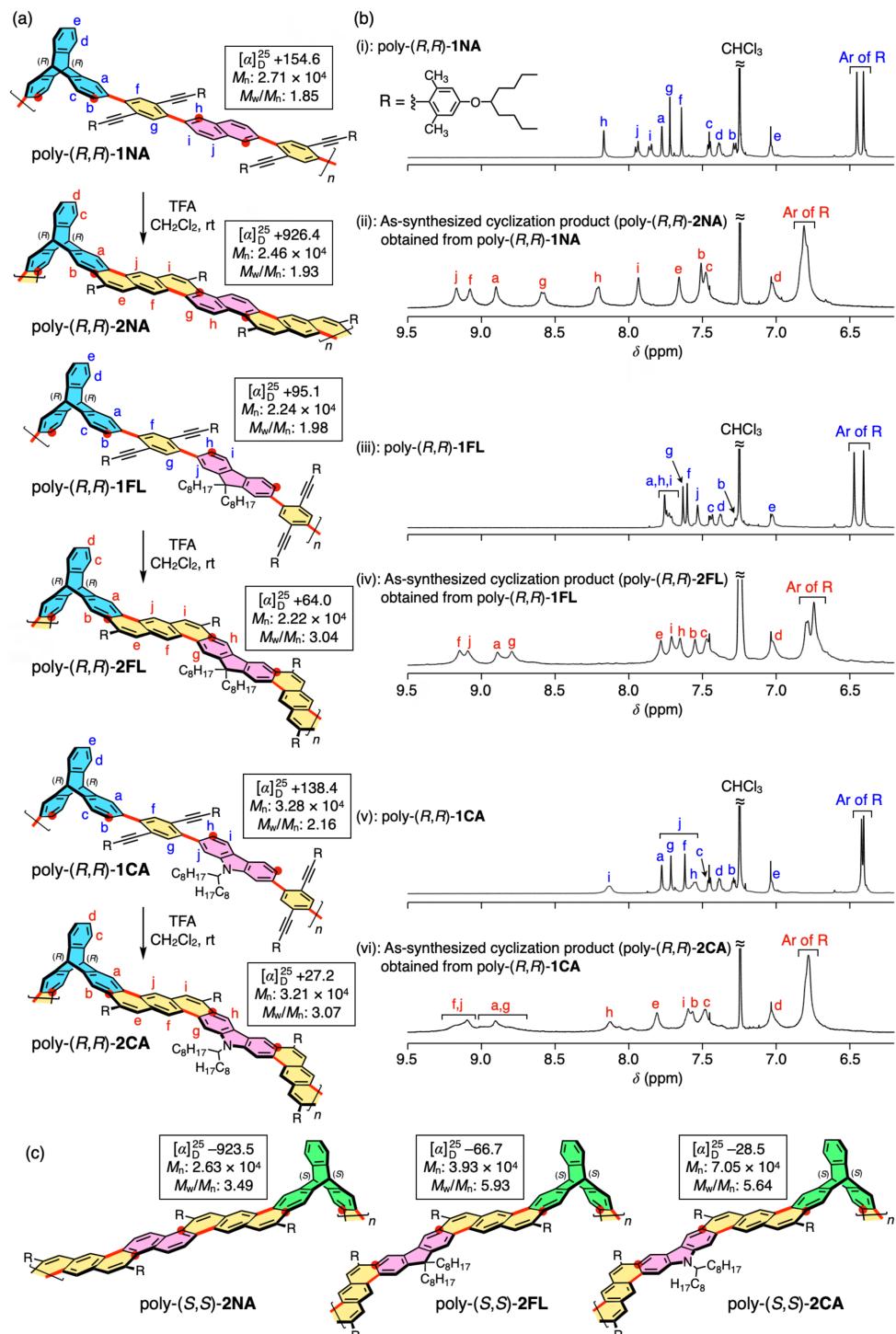


Figure 2 (a) Synthesis of one-handed helical ladder polymers, poly-(R,R)-2NA (top), poly-(R,R)-2FL (middle), and poly-(R,R)-2CA (bottom), through acid-promoted alkyne benzannulations of their precursor polymers (poly-(R,R)-1NA, poly-(R,R)-1FL, and poly-(R,R)-1CA, respectively). (b) ^1H NMR spectra (500 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.

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,R*)- and (*S,S*)-**2NA**, poly-(*R,R*)- and (*S,S*)-**2FL**, and poly-(*R,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 model compounds containing the 2,6-linked-tritycene,³³ 2,6-linked-naphthalene,³⁵ 2,7-linked-fluorene,³⁵ and 2,7-linked-carbazole units proceeded in a quantitative and perfect chemoselective manner without any side reactions (Figures S8–S11). To the best of our knowledge, poly-(*R,R*)- and (*S,S*)-**2CA** are the first one-handed helical ladder polymers with the nitrogen-containing heteroaromatic rings in the main chain synthesized through alkyne benzannulations.³⁸

The possible helical ladder structures of a series of (*R,R*)-tritycene-bound helical ladders, poly-(*R,R*)-**2NA**, poly-(*R,R*)-**2FL**, and poly-(*R,R*)-**2CA**, with 12 repeating units optimized by molecular mechanics calculations are shown in Figure 3. Unlike the previously reported (*R,R*)-tritycene-bound poly-(*R,R*)-**A** with the (*P*)-handed contracted tubular helical structure having a helical pitch and diameter of ca. 1.5 and 2 nm, respectively,³³ poly-(*R,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,R*)-**2FL** and poly-(*R,R*)-**2CA** (Figure 3b,c). These results indicated that the 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**³³ with the absorption edges of ca. 400 nm or less, resulting from the more planar and extended π -conjugated repeating units. In particular, the absorption edge of poly-**2CA** was extended to over 450 nm (Figure 4c (ii, iv)) due to the electron-donating carbazole segment with a 14 π -electron aromatic system that can narrow the optical bandgap.^{39,40} The optical rotation value of poly-(*R,R*)-**2NA** significantly increased compared to that before ladderization as observed for poly-(*R,R*)-**A**, whereas 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 (iv) 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

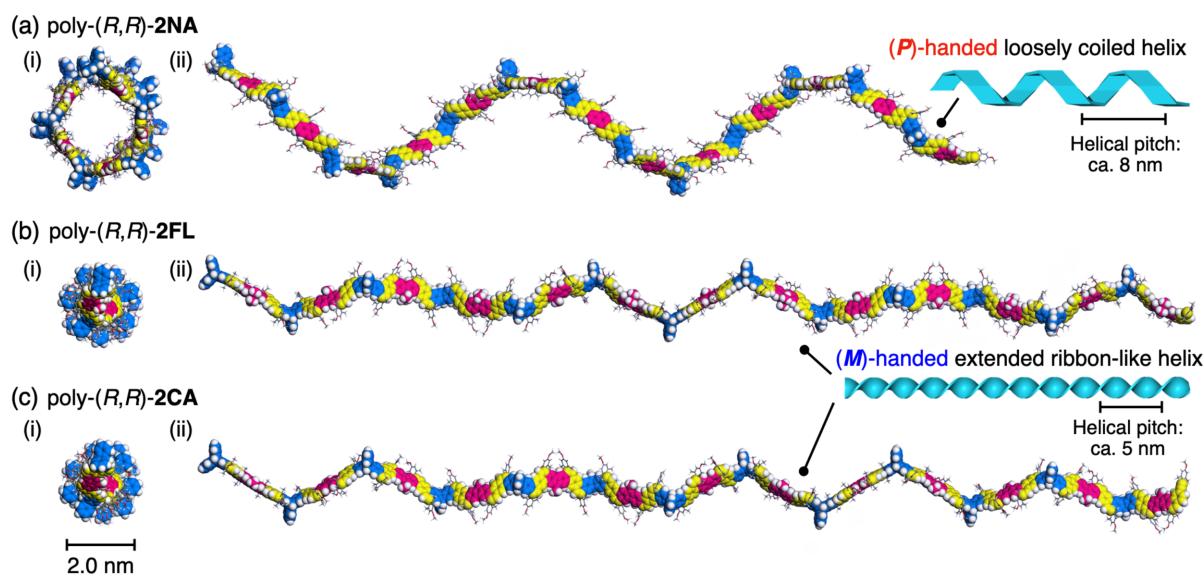


Figure 3 Top (i) and side (ii) views of right (*P*)-handed helical poly-(*R,R*)-**2NA** (a) and left (*M*)-handed helical poly-(*R,R*)-**2FL** (b) and poly-(*R,R*)-**2CA** (c) structures with 12 repeating units optimized by molecular mechanics (MM) calculations (Compass II force field). For simplicity, 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 π -conjugated ladder frameworks are colored in blue, pink, and yellow, respectively.

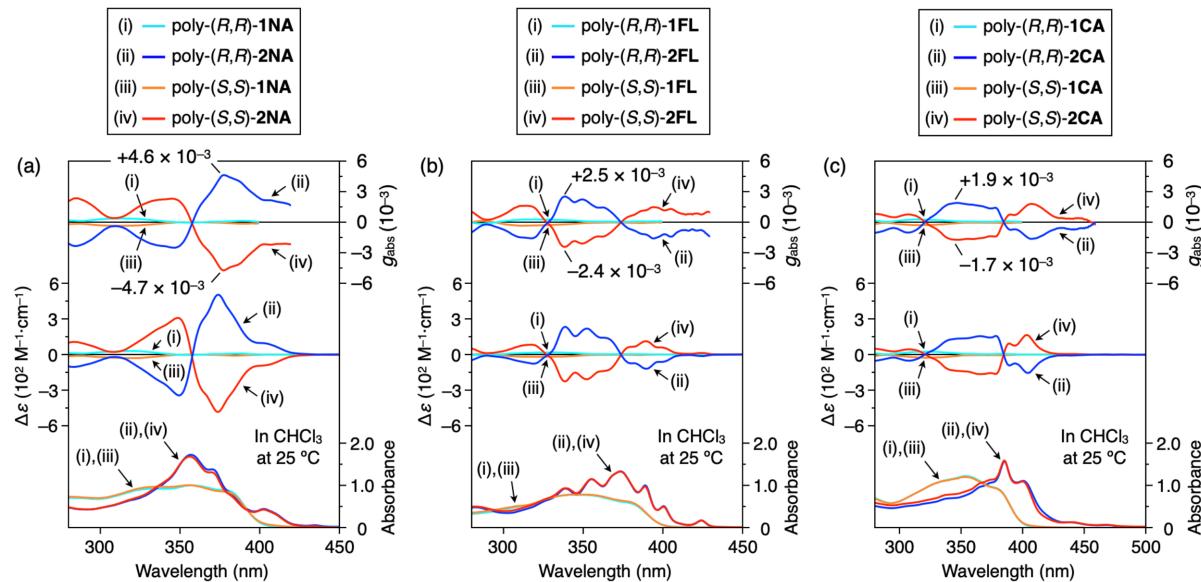


Figure 4 Absorption, CD, and Kuhn's dissymmetry factor (g_{abs}) spectra of (R,R)- and (S,S)-tryptcene-bound precursor and ladder polymers containing naphthalene- (a; poly-(R,R)-1NA (i), poly-(R,R)-2NA (ii), poly-(S,S)-1NA (iii), and poly-(S,S)-2NA (iv)), fluorene- (b; poly-(R,R)-1FL (i), poly-(R,R)-2FL (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^{-4} M.

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)-**A**³³ 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)- and (S,S)-**2NA** showed the most intense CD signals and its Kuhn's dissymmetry factor ($|g_{\text{abs}}|$) 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** ($|g_{\text{abs}}| = 5.0 \times 10^{-3}$)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 π -extended achiral segments incorporated in the main chain in chloroform under irradiation at 365 nm and their absolute quantum yields (Φ_F) 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

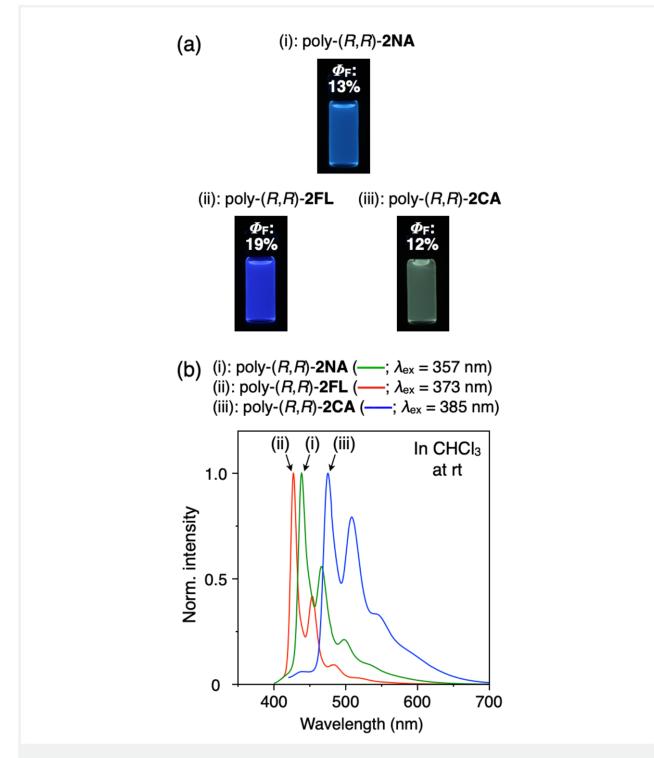


Figure 5 (a) Photographs of poly-(R,R)-2NA (i), poly-(R,R)-2FL (ii), and poly-(R,R)-2CA (iii) in chloroform under irradiation at 365 nm. Fluorescence quantum yields (Φ_F) are also shown. (b) Normalized PL spectra of poly-(R,R)-2NA (i), poly-(R,R)-2FL (ii), and poly-(R,R)-2CA (iii) in chloroform at room temperature. [Repeating units of polymer] = 1.0×10^{-5} M.

Conclusions

In summary, we have succeeded in modulating the secondary structures of the (*R,R*)- and (*S,S*)-tritycene-based one-handed helical ladder polymers simply by replacing the π -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 “ π -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

Supporting Information for this article is available online at <https://doi.org/10.1055/a-2208-4389>.

Conflict of Interest

The authors declare no conflict of interest.

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- (37) **General procedure:** The one-handed helical ladder polymers were prepared by alkyne benzannulations of the corresponding precursor polymers. 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 μ mol) 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/trifluoroacetic acid 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 meth-

anol, and dried in vacuo to yield poly-(*S,S*)-**2NA** as a brown solid (4.0 mg, >99% yield). $[\alpha]^{25}_{D} -923.5$ (*c* 0.057, CHCl_3). ^1H NMR (500 MHz, CDCl_3 , 50 °C): δ 9.30 – 9.12 (br, 2 H, Ar–H), 9.12 – 8.95 (br, 2 H, Ar–H), 8.95 – 8.75 (br, 2 H, Ar–H), 8.70 – 8.45 (br, 2 H, Ar–H), 8.35 – 8.10 (br, 2 H, Ar–H), 8.05 – 7.85 (br, 2 H, Ar–H), 7.75 – 7.60 (br, 2 H, Ar–H), 7.60 – 7.35 (br, 4 H, Ar–H), 7.10 – 6.95 (br, 2 H, Ar–H), 6.95 – 6.60 (br, 8 H, Ar–H), 5.85–5.65 (br, 2 H, CH), 4.50 – 4.20 (br, 4 H, CH), 2.20 – 1.65 (br, 40 H, CH_2 , CH_3), 1.65 – 1.20 (br, 32 H, CH_2), 1.10–0.80 (br, 24 H, CH_3).

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