Electronic Supplementary Information

Pre-regulation of the Planar Chirality of Pillar[5]arenes for Preparing Discrete Chiral Nanotubes

Shixin Fa, Keisuke Adachi, Yuuya Nagata, Kouichi Egami, Kenichi Kato, and Tomoki Ogoshi*
Table of Contents

General ................................................................................................................................................. 1
Syntheses ............................................................................................................................................... 1
CD silencing of 1 .................................................................................................................................. 5
CD awakening of 1 ................................................................................................................................. 9
Chirality regulation of 1 by DBB and DCE ......................................................................................... 11
Nanotube formation of 1 and 2 ............................................................................................................ 14
Chirality storage of the nanotubes after drying .................................................................................. 20
Supplementary discussion .................................................................................................................... 21
References ............................................................................................................................................. 22
$^1$H & $^{13}$C NMR Spectra .................................................................................................................... 23
General

All commercially available reagents and solvents were used as received. $^1$H NMR and $^{13}$C NMR spectra were recorded on JEOL JNM-ECS400, JNM-ECZ500R and JNM-ECA600P spectrometers at room temperature. Chemical shifts were reported in ppm versus tetramethylsilane. COSY and NOESY experiments were performed on JEOL JNM-ECA600P spectrometer at 30 °C. UV-vis absorption spectra and circular dichroism (CD) spectra were recorded at 20 °C on JASCO V-750 spectrophotometer and JASCO J-1500 CD spectrometer, respectively. 2 mm quartz cuvets were used for both UV-vis and CD measurements. High-resolution ESI-MS was recorded on Thermo Fisher Scientific Exactive Plus mass spectrometer equipped with UltiMate 3000 HPLC. DFT calculations for structures of 1 with and without intramolecular hydrogen bond network (HBN) were carried out at $\omega$B97XD/6-31G(d,p) level of theory using Gaussian 16 Rev C.01. The initial geometry was generated according to the single crystal X-ray diffraction analysis of a pillar[5]arene having benzoic acid moieties and n-butyloxyl chains and the addition of water molecules.

Syntheses

Synthesis of peralkylamino-substituted pillar[5]arene 2$^2$ and compound 5$^1$ was followed reported procedure with optimization.

Scheme S1. Synthesis of rim-differentiated pillar[5]arene 1.
**Compound 6.** To a mixture of tosylate 5 (17.5 g, 72.4 mmol) and potassium carbonate (20.0 g, 145 mmol) in DMF (100 mL) under 0 °C was added 2,5-dihydroxybenzaldehyde (10.0 g, 72.4 mmol). The mixture was stirred in ice bath for another 1 h, and then was allowed to stir at room temperature for 12 h. The solid was filtered off, and the filtrate was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (450 mL), washed with brine (50 mL), and dried over sodium sulfate. The solid was filtered off. After removal of the solvent, the residue was chromatographed on a silica gel column using a mixture of n-hexane and ethyl acetate (from 10:1 to 5:1, v/v) as the mobile phase. Compound 6 was obtained as yellow oil (2.20 g, 10.6 mmol, 15%).

\[ \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta 10.46 (s, 1H), 7.34 (d, J = 2.8 Hz, 1H), 7.09 (dd, J = 3.5, 3.0 Hz, 1H), 6.90 (d, J = 3.5 Hz, 1H), 5.31 (s, 1H), 3.90 (dd, J = 6.0, 9.0 Hz, 1H), 3.81 (dd, J = 5.5, 8.5 Hz, 1H), 1.91 (m, 1H), 1.57 (m, 1H), 1.31 (m, 1H), 1.04 (d, J = 7.0 Hz, 2H), 0.96 (t, 3H). \]

\[ \text{13C NMR (125 MHz, CDCl}_3\text{): } \delta 190.0, 156.6, 149.5, 125.3, 123.6, 114.4, 113.4, 73.9, 34.9, 26.2, 16.7, 11.4. \]

ESI-HRMS. Calcd for C\(_{12}\)H\(_{16}\)O\(_3\) (m/z): [M + H]\(^+\), 209.1172. Found: 209.1171.

**Compound 7.** To a stirred solution of mono-substituted dihydroxybenzaldehyde 6 (4.79 g, 23.0 mmol) in acetonitrile (230 mL) was added methyl 4-(bromomethyl) benzoate (5.27 mg, 23.0 mmol) and potassium carbonate (3.82 g, 27.6 mmol). The reaction mixture was stirred under reflux for 2 h. After cooled down to room temperature, the solid was filtered off, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column using a mixture of n-hexane and acetone (from 10:1 to 5:1, v/v) as the mobile phase. Compound 7 was obtained as yellow oil (7.63 g, 21.0 mmol, 93%).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta 10.50 (s, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 3.6 Hz, 1H), 7.19 (dd, J = 3.4, 9.0 Hz, 1H), 6.94 (d, J = 9.2 Hz, 1H), 5.11 (s, 2H), 3.92 (s, 3H), 3.91-3.81 (m, 2H), 1.92 (m, 1H), 1.63-1.52 (m, 1H), 1.37-1.25 (m, 1H), 1.05 (d, J = 3.0 Hz, 3H), 0.96 (t, 3H). \]

\[ \text{13C NMR (125 MHz, CDCl}_3\text{): } \delta 189.6, 166.9, 156.9, 152.3, 142.0, 130.0, 129.8, 127.1, 125.2, 124.4, 114.4, 111.5, 73.9, 70.0, 52.2, 34.9, 26.2, 16.7, 11.4. \]

ESI-HRMS. Calcd for C\(_{21}\)H\(_{24}\)O\(_5\) (m/z): [M + Na]\(^+\), 379.1516. Found: 379.1523.

**Compound 3.** To a stirred solution of di-substituted dihydroxybenzaldehyde 7 (7.63 g, 21.0 mmol) in methanol (70.0 mL) at 0 °C, sodium borohydride (976 mg, 25.7 mmol) was carefully added. The ice bath was removed, and the mixture was stirred at room temperature for 1 h. Brine (50 mL) was carefully added to quench the reaction. The mixture was extracted with dichloromethane (2 × 50 mL). The organic phase was combined and washed with water (50 mL) and brine (50 mL), and dried over anhydrous sodium sulfate. The solid was then filtered off. The filtrate was concentrated under reduced pressure to give compound 3 obtained as yellow oil (4.86 g, 13.5 mmol, 65%).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta 8.04 (dd, J = 6.6, 1.8 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 2.7 Hz, 1H), 6.83-6.76 (m, 2H), 5.08 (s, 2H), 4.67 (d, J = 6.4 Hz, 2H), 3.92 (s, 3H), 3.85-3.73 (m, 2H), 2.37 (t, J = 6.5 Hz, 1H), 1.90-1.83 (m, 1H), 1.60-1.50 (m, 1H), 1.35-1.24 (m, 1H), 1.03 (d, J = 6.8 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 189.6, 166.9, 156.9, 152.3, 142.0, 130.0, 129.8, 127.1, 114.3, 112.1, 73.4, 70.2, 62.4, 52.3, 35.0, 26.4, 16.9, 11.5. \]

ESI-HRMS. Calcd for C\(_{21}\)H\(_{26}\)O\(_5\) (m/z): [M + Na]\(^+\), 381.1672. Found: 381.1676.

**Compound 4.** To a stirred solution of di-substituted dihydroxybenzyl alcohol 3 (1.62 g, 4.50 mmol) in 1,2-dichloroethane (720 mL) was added anhydrous iron (III) chloride (77.0 mg, 0.473 mmol). The mixture was stirred at room temperature for 16 h before methanol (100 mL) was
added to quench the reaction. After concentrated under reduced pressure, the residue was chromatographed on a silica gel column using a mixture of n-hexane and acetone (10:1, v/v) as the mobile phase. The obtained white solid was further purified by thoroughly washing with a mixture of n-hexane and 2-propanol (99:1, v/v). Compound 4 was obtained as white solid (107 mg, 0.063 mmol, 7%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (dd, $J = 8.3$, 2.1 Hz, 10H), 7.35 (dd, $J = 8.2$, 3.7 Hz, 10H), 6.87-6.83 (m, 10H), 4.59-4.49 (m, 10H), 3.90-3.80 (m, 5H), 3.63-3.52 (m, 10H), 1.92-1.89 (m, 5H), 1.68-1.52 (m, 5H), 1.34-1.29 (m, 5H), 1.12 (d, $J = 6.6$ Hz, 7.4H), 1.06 (d, $J = 6.8$ Hz, 7.8H), 0.96 (dt, $J = 7.5$, 1.6 Hz, 15H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.9, 150.8, 150.7, 149.4, 149.3, 143.3, 129.9, 129.6, 128.7, 128.4, 127.2, 127.1, 115.4, 115.2, 73.8, 73.7, 69.8, 52.3, 35.6, 35.5, 29.7, 26.6, 17.2, 16.9, 11.7, 11.6. APCI-HRMS. Calcd for C$_{105}$H$_{121}$O$_{20}$ (m/z): [M + H]$^+$, 1701.8446. Found: 1701.8404.

**Compound 1.** To the pillar[5]arene ester 4 (149 mg, 0.088 mmol) in tetrahydrofuran (2.2 mL), sodium hydroxide (105 mg, 2.63 mmol) in water (2.2 mL) was added dropwise. The mixture was refluxed for 24 h. After the organic solvent was removed under reduced pressure, the solution was poured into aqueous HCl solution (1 M, 60 mL). The precipitate was collected by filtration, and washed with water (600 mL). After drying in vacuum, the product was obtained as white solid (137 mg, 0.084 mmol, 95%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.02-7.95 (m, 10H), 7.29-7.24 (m, 10H), 6.90-6.80 (m, 10H), 4.73-4.35 (m, 10H), 3.86-3.56 (m, 20H), 1.91-1.24 (m, 30H), 1.13 (t, $J = 6.5$ Hz, 7.4H), 1.06 (t, $J = 7.0$ Hz, 7.4H), 0.98-0.91 (m, 15H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ 191.13, 167.07, 149.49, 148.32, 142.13, 130.37, 129.47, 127.82, 127.71, 126.84, 113.99, 113.92, 73.10, 72.92, 68.49, 34.90, 34.71, 28.89, 25.85, 25.75, 16.60, 16.23, 11.23. APCI-HRMS. Calcd for C$_{100}$H$_{110}$O$_{20}$ (m/z): [M + H]$^+$, 1631.7663. Found: 1631.7621.

To confirm that the chirality information of 1 observed on CD spectra was ascribed to planar chirality, monomeric compound 10 was synthesized by following the procedure shown in Scheme S2. Synthesis of the precursor 8 was followed literature.²

**Scheme S2. Synthesis of monomer 10.**

**Compound 9.** To a stirred solution of mono-substituted dihydroxybenzene 8 (102 mg, 0.57 mmol) in acetonitrile (10 mL) was added methyl 4-(bromomethyl) benzoate (156 mg, 0.68 mmol) and potassium carbonate (94 mg, 0.68 mmol). The reaction mixture was stirred under reflux for 2 h. After cooled down to room temperature, the solid was filtered off. The filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column using a mixture of n-hexane and acetone (from 10:1 to 5:1, v/v) as the mobile phase. Compound 9 was obtained as yellow oil (86.0 mg, 0.26 mmol, 48%). $^1$H NMR (600 MHz,
CDCl₃: δ 8.04 (d, :Event 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 6.89-6.81 (m, 4H), 5.07 (s, 2H), 3.92 (s, 3H), 3.76 (dd, J = 9.1, 6.1 Hz, 1H), 3.68 (dd, J = 9.1, 6.6 Hz, 1H), 1.86-1.80 (m, 1H), 1.59-1.52 (m, 1H), 1.28-1.21 (m, 1H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 154.1, 152.6, 142.8, 130.0, 129.7, 127.2, 116.0, 115.6, 73.7, 70.3, 52.3, 34.9, 26.3, 16.7, 11.5. APCI-HRMS. Calcd for C₂₀H₂₄O₄ (m/z): [M + CH₂ + H]⁺, 343.1904. Found: 343.1910.

**Compound 10.** To a stirred solution of di-substituted dihydroxybenzene 9 (80 mg, 0.244 mmol) in tetrahydrofuran (5 mL), sodium hydroxide (8 mg, 0.300 mmol) in water (5 mL) was added dropwise. The mixture was refluxed for 24 h. After the solvent was removed under reduced pressure, the solution was poured into aqueous HCl solution (1 M, 5 mL). The precipitate was collected by filtration, and washed with water (50 mL). After drying in vacuum, the product was obtained as white solid (67 mg, 0.212 mmol, 88%). ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 6.90-6.82 (m, 4H), 5.08 (s, 2H), 3.79-3.66 (m, 2H), 1.89-1.79 (m, 1H), 1.61-1.51 (m, 1H), 1.30-1.19 (m, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 171.1, 154.1, 152.6, 143.8, 130.7, 128.7, 127.2, 116.0, 115.6, 73.7, 70.2, 35.0, 26.3, 16.7, 11.5. APCI-HRMS. Calcd for C₁₉H₂₂O₄ (m/z): [M + H]⁺, 315.1591. Found: 315.1592.
CD silencing of 1

Fig. S1 UV spectra of 1 (0.1 mM), 10 (0.5 mM), 11 (0.1 mM), and 12 (0.125 mM) in chloroform at 20 °C.

Fig. S2 CD and UV spectra of 1 (0.1 mM) upon heating in chloroform.
Fig. S3 Partial 2D NOESY NMR spectrum (600 MHz, CDCl₃, 303 K, top) and 2D COSY NMR spectrum (600 MHz, CDCl₃, 303 K, bottom) of 1 (0.1 mM).
Fig. S4 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$) of (a) 4 (0.1 mM) and (b) 1 (0.1 mM) at 20 °C. Rim-differentiated pillar[5]arene 4 possesses five asymmetric carbon centers on rims, so there are two sets of peaks on $^1$H NMR spectrum, which are ascribed to the two diastereomers ($S$,$S$,$S$,$S$, $pS$,$pS$,$pS$,$pS$)- and ($S$,$S$,$S$,$S$, $pR$,$pR$,$pR$,$pR$)-4 (Fig. S3a, ($pS$)- and ($pR$)- 4 in short). By contrast, four sets of resonance appear on $^1$H NMR spectrum of 1. In especial, there are eight peaks altogether in the region of H$_d$ and H$_e$. Compared with 4, the molecular structure of 1 has five benzoic acid groups on one rim, which tend to form intramolecular HBN mediated by water molecules,$^2$ resulting in slow rotation of the units of 1 on NMR time scale.
Fig. S5 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$) of 1 recorded at various temperatures. Increasing the temperature from 30 °C to 60 °C, slight coalescence was observed.

Fig. S6 Partial $^1$H NMR spectra of 1 (0.1 mM, 400 MHz) in various solvents. In polar solvents (e.g., methanol-$d_4$ and acetone-$d_6$), only one set of peaks was observed, indicating that the free rotation of the units was fast on NMR time scale. The HBN was completely broken. In nonpolar solvent (i.e., dichloromethane-$d_2$), the $^1$H NMR spectrum was similar to that in CDCl$_3$, due to the slow unit rotation.
Fig. S7 Geometrical structures and intermolecular interactions of (a) $pS\cdot 1$ without HBN and (b) $pS\cdot 1$ with HBN mediated via five water molecules obtained from DFT ($\omega$B97XD/6-31G(d,p)) optimization.

CD awakening of 1

Fig. S8 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$) of 1 (0.1 mM) upon addition of methanol-$d_4$. The total volume of CDCl$_3$ was 500 $\mu$L in all cases. Upon addition of methanol-$d_4$, the four sets of resonance coalesced gradually, because methanol is efficient to cut the HBN by forming hydrogen bonds with benzoic acid groups (i.e., solvation). When ca. 2% of methanol-$d_4$ was added, the four sets of peaks coalesced to one set of broad peaks, indicating that the free rotation of the units in 1 was initiated.
**Fig. S9** CD and UV spectra of 1 (0.1 mM) upon heating in chloroform in the presence of 10\% of methanol.

**Fig. S10** Partial $^1$H NMR spectra of 1 (0.1 mM, 400 MHz) without (top) and with (bottom) 10\% of methanol-$d_4$. The diastereomeric excesses were obtained by integrating the $pS$- and $pR$-forms of proton signals of H$_i$. 
Chirality regulation of 1 by DBB and DCE

Fig. S11 Partial $^1$H NMR spectra of 1 (0.1 mM, 400 MHz) with methanol-$d_4$ (10% of the volume fraction) and DBB (5 equiv., top) and DCE (35 equiv., bottom). The diastereomeric excesses were obtained by integrating the $pS$- and $pR$-forms of proton signals of $H_i$.

Discussion on complexation of 1 with DBB and DCE (Fig. S12).

We tried to cultivate single crystals of the complexes between 1 with DBB and DCE to understand the interaction details in these complexes. Unfortunately, we failed to obtain high-quality single crystal available to analyze by X-ray diffraction. However, our recent work (Chem. Commun., 2020, 56, 8424–8427), in which we have observed the achiral solvent-dependent CD-signal change of planar chiral pillar[5]arene 13 (Fig. S12), can help us to understand the mechanism of the planar chiral further induction and inversion of 1.

Pillar[5]arene 13 has the same chiral substituents as 1 on two rims, and showed positive and negative Cotton effects in DCE and DBB, respectively (Chem. Commun., 2020, 56, 8424–8427). These observations are same as that in our current research. In our current research, addition of DCE in the CD-awakened 1 resulted in positive CD signal of 1, while addition of DBB in CD-awakened 1 caused further negative CD signal (Fig. 3 in the main text).

In Fig. S12, we showed the single crystalline structures of the 1:1 host-guest complex of 13 and DBB, and 13 and DCE.

In the complex of 13 and DBB, the DBB molecule is long enough to repel the third carbon atom (i.e., carbons $\gamma$ and $\varepsilon$) on each substituent (Figure S12c). Thus, the bulky ethyl branch (carbons $\gamma$ and $\delta$ in cyan color) on aliphatic chains are located out of the cavity to minimize the steric hindrance between the bromine atoms of DBB and aliphatic chains, which resulted in a tendency of $pS$ induction of 13. Thus, the complex of 13 and DBB in crystalline state only shows $pS$ chirality. In other words, the ($S,S,S,S,pS,pS,pS,pS,pS$)-form of 13 are more stable.
than (S,S,S,S,pR,pR,pR,pR,pR)-form when complexing with DBB. Because of the same chiral substituents in 1 and 13, we believe that complexation of DBB and 1 also leads a pS-favoring rotation of 1.

In contrast, with short length, DCE is fully buried into the central part of the pillar[5]arene’s cavity without interrupting the substituents on rims (Figure S12d). As a consequence, enough space is made in the cavity for the ethyl branch (carbons γ and δ in cyan color) on aliphatic chains, leading a (S,S,S,S,pR,pR,pR,pR,pR)-form of 13. Similarly, we believe that complexation with DCE also leads a pR-favoring rotation of 1, which make the CD conversion of 1.

Discussion on chirality regulation of 1 by DBB and DCE in absence of MeOH. Different from the cases of planar chirality awakening 1, the planar chiral induction effect was very weak when guest molecules were directly added to the solution of 1 in chloroform without awakening the chirality in advance (Fig. 3b). Addition of DBB induced ca. 30% of the CD intensity of chirality-silenced 1 compared with the chirality-awakened 1. DCE failed to induce the planar chirality of 1 in absence of MeOH.

The weak chiral induction of 1 on addition of DBB was caused by the dimerization of 1 as evidenced by the appearance of the dimer peaks on 1H NMR spectra (Fig. S13-S14). To form dimers, the intramolecular HBNs would be broken and rearranged to intermolecular HBNs, which provided a chance for the unit rotation of 1, thus induced its planar chirality to

Fig. S12 Single crystal structures of compound 13 complexed with (a,c) DBB and (b,d) DCE. The two branches of the aliphatic chains on rims of 13 were shown in different colors. Data were taken from ref. 4.
some extent. In contrast, DCE cannot trigger the dimerization of 1 even in a much excess amount (Fig. S14). The different effect on dimerization of 1 on addition of DBB and DCE is also ascribed to the length-effect of the guest molecules (Fig. S12). DCE may be fully buried into the central part of the pillar[5]arene’s cavity without interrupting the intramolecular HBN on rims, while DBB is long enough to influence the groups on rims. Nevertheless, awakening the planar chirality of 1 via MeOH in advance was important to launch an effective chiral regulation.

**Fig. S13** Partial $^1$H NMR spectra (600 MHz, CDCl$_3$) of 1 at various concentrations. At diluted concentrations (0.1–0.5 mM), no change was observed on $^1$H NMR spectra. As the concentration increased to 1.5 mM and higher, a new set of peaks emerged (H$_a$ (dimer) and H$_b$ (dimer)), which implied that self-assemblies formed as concentration was increased. Similar behavior has been observed in our previous work,$^2$ where evidences demonstrated the concentration-dependent dimerization of compounds similar to 1 via intermolecular hydrogen bonds. Therefore, we assigned the emerging peaks as dimers of 1.

**Fig. S14** Partial $^1$H NMR spectra of 1 (0.1 mM) with DBB (5 equiv.) and DCE (35 equiv.) in CDCl$_3$ at 20 °C. Upon addition of 5 equiv. of DBB in the solution of 1 (0.1 mM), all monomeric 1 was dimerized. By contrast, even 35 equiv. of DCE was not able to trigger the dimerization of 1. The different effect on dimerization of 1 on addition of DBB and DCE is ascribed to the length-effect of the guest molecules. As mentioned above (Fig. S12), the DBB molecule is long...
enough to repel the third carbon atom on each substituent. This will surely interrupt the intramolecular HBN on the other rim of 1. As a consequence, the stability of the intramolecular HBN decrease, which gives a chance for dimerization of 1 by forming intermolecular hydrogen bonds. In contrast, DCE is fully buried into the central part of the pillar[5]arene’s cavity without interrupting the intramolecular HBN on rims.

**Nanotube formation of 1 and 2**

![1H NMR spectra](image)

**Fig. S15** (a) 1H NMR spectra of 1 (0.1 mM), 2 (0.05 mM) and the trimeric nanotubes via mixing 1 (0.1 mM) and 2 (0.05 mM) in CDCl3. Mixing 1 and 2 with a 1:2 ratio resulted in clear and simple 1H NMR spectrum. This suggested the formation of a single species 1₂·2 in solution.
Fig. S16 DOSY spectrum (600 MHz, CDCl$_3$, 30 ℃) of the mixture of 1 (0.1 mM) and 2 (0.05 mM) with DBB (0.5 mM). The identical diffusion constants of the peaks on both 1 and 2 indicated that 1 and 2 assembled into a single component in solution, which confirmed the formation of trimeric nanotubes.

Fig. S17 Experimental and calculated electrospray ionization peaks of the trimeric nanotube (1$_2$·2).
**Fig. S18** CD and UV spectra of trimeric nanotubes prepared by pre-regulation strategy (Path A in Fig. 4) upon heating and cooling.

**Fig. S19** CD and UV spectra of $pS$- and $pR$-rich trimeric nanotubes prepared by pre-regulation strategy.
Fig. S20 Possible structures of chiral trimeric nanotubes. There are six possible combinations of 1 and 2 in trimeric nanotubes. However, structures (II), (III), (IV) and (V) would be less stable than (I) and (VI), because steric hindrance between the neighboring pillar[5]arenes with opposite planar chirality may decrease the stability of the trimeric structures as what observed in our previous research.\textsuperscript{2} Therefore, upon addition of 0.5 equiv. of 2 in the pre-regulated 1 (i.e., 1 + MeOH + DBB and 1 + MeOH + DCE), the resulted nanotubes would mainly adopt forms (I) and (VI), respectively.

Fig. S21 CD and UV spectra of trimeric nanotubes prepared by post-regulation strategy (Path B in Fig. 4) upon heating and cooling.
Fig. S22 CD spectra of (a) the trimeric nanotubes prepared from partially regulated 1 (0.1 mM) and (b) upon further adding MeOH (10% volume fraction of the solution) (Path C in Fig. 4).

Fig. S23 Pre-regulation of 1 for preparing pR-rich nanotubes (Path A in Fig. S26). CD changes of 1 (0.1 mM) upon addition of MeOH (10% volume fraction of the solution), DCE (35 equiv.) and 2 (0.5 equiv.) by the illustrated sequence.
Fig. S24 Path B in Fig. S26. CD changes of 1 (0.1 mM) upon addition of 2 (0.5 equiv.), MeOH (10% volume fraction of the solution) and DCE (5 equiv.) by the illustrated sequence.

Fig. S25 Path C in Fig. S26. CD changes of 1 (0.1 mM) upon addition of DCE (35 equiv.), 2 (0.5 equiv.) and MeOH (10% volume fraction of the solution) by the illustrated sequence.
Fig. S26 Illustration of pR-rich nanotubes prepared by pre- and post-regulation strategies.

Fig. S27 A summary of the pre- and post-regulation results. (a) CD spectra of pS-rich nanotubes constructed from 1 (0.1 mM), 2 (0.5 equiv.), MeOH (10% volume fraction of the solution), and DBB (5 equiv.) in different sequences (Fig. 4 and S22). (b) CD spectra of pR-rich nanotubes constructed from 1 (0.1 mM), 2 (0.5 equiv.), MeOH (10% volume fraction of the solution), and DCE (35 equiv.) in different sequences (Fig. S23-26).
Chirality storage of the nanotubes after removing awakener and regulators

By removing the solvent and heating the pre-regulated nanotubes at 120 °C for 5 days in vacuum, we tried to remove all external factors (i.e., methanol, DBB and DCE) that was used to regulate the chirality of 1. By analyzing the ^1H NMR spectra before and after heating, we found that all the external factors (methanol and DBB) in the pS-rich nanotubes prepared by path A were removed (Fig. S28). The pR-rich nanotubes prepared by pre-regulation show weak CD signals. After removal of DCE and methanol, the CD changes were difficult to monitor. Therefore, we only checked the stability of the aforementioned pS-rich nanotubes after removing external factors in solution by CD measurement (Fig. S29).

Fig. S28 Partial ^1H NMR spectra of pS-rich nanotubes (0.05 mM, CDCl3) prepared by path A (top) and after heating the sample in vacuum at 120 °C for 5 days (bottom). DBB was completely removed as evidenced by the disappearance of the DBB proton signals after heating.
**Fig. S29** Time-dependent normalized CD spectra (chloroform, 20 °C) of the $\mu$S-rich nanotubes prepared by path A after removing DBB and methanol.
Supplementary discussion

**Fig. S30** Optimization of the charge amount of **DBB**. The CD spectra (CHCl$_3$) of 1 (0.1 mM) upon addition of **DBB** (0 - 10 equiv.) were recorded at 20 °C. The CD intensity slightly changed upon addition of **DBB** from 1 to 5 equiv.; on further addition of **DBB**, the CD changes were negligible. Thus, 5 equiv. of **DBB** was chosen for all other experiments in this research.

**Fig. S31** Optimization of the charge amount of **DCE**. The CD spectra (CHCl$_3$) of 1 (0.1 mM) with MeOH (10% volume fraction of the solution) upon addition of **DCE** (0 - 35 equiv.) were recorded at 20 °C. Upon addition of **DCE**, the CD intensity gradually increased until 35 equiv. of **DCE** was added. Thus, 35 equiv. of **DCE** was chosen for all other experiments in this research.
Fig. S32 CD spectra (CHCl₃) of 10 (0.1 mM, orange line) upon addition of 25 equiv. of DBB (blue line) and 125 equiv. of DCE (green line). No CD signals were observed upon addition of linear guests. It is clear that the macrocyclic structure was essential for chiral induction upon addition of linear guests.

References

1. Gaussian 16, Revision C.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
2. S. Fa, Y. Sakata, S. Akine and T. Ogoshi, Angew. Chem. Int. Ed., 2020, 59, 9309–9313.
3. K. Mori, T. Tashiro, B. Zhao, D. Suckling and A. El-Sayed, Tetrahedron, 2010, 6, 2642–2653.
4. Y. Nagata, M. Suzuki, Y. Shimada, H. Sengoku, S. Nishida, T. Kakuta, T. Yamagishi, M. Suginome and T. Ogoshi, Chem. Commun., 2020, 56, 8424–8427.
$^{1}H$ & $^{13}C$ NMR Spectra

[Diagram of the NMR spectra with chemical shifts and peak intensities]
