A Tautoleptic Approach to Chiral Hydrogen-Bonded Supramolecular Tubular Polymers with Large Cavity

Algirdas Neniškis,[a] Dovilė Račkauskaitė,[a] Qixun Shi,[b] Aiden J. Robertson,[c] Andrew Marsh,[c] Artūras Ulčinas,[d] Ramūnas Valiokas,[d] Steven P. Brown,[c] Kenneth Wärnmark,*[b] and Edvinas Orentas*[a, d]
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Materials and Methods

All chemicals were used as received from commercial suppliers. Compounds 1a\(^1\) and 1b\(^2\) were prepared according to reported procedures. All moisture sensitive reactions were carried out under an atmosphere of dry nitrogen or argon using oven-dried glassware. Anhydrous tetrahydrofuran was distilled from benzophenone-sodium, dichloromethane was distilled from calcium hydride and toluene was distilled from sodium. Yields refer to chromatographically and spectroscopically homogeneous materials. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light (general), aq. KMnO\(_4\) solution (for unsaturated compounds) and vanilin solution (general). For beta-ketoesters, ferric chloride (FeCl\(_3\)) alcohol solution was used as selective developing agent. Flash column chromatography was performed on Merck silica gel (60, particle size 0.0430-0.663 mm). Melting points were recorded with a Gallenkamp apparatus and are not corrected. \(^1\)H and \(^13\)C spectra were recorded on Bruker 400 MHz spectrometer. Chemicals shifts are given in parts per million, relative to TMS using the residual solvent peaks at \(\delta = 7.27\) (\(^1\)H NMR) and 77.06 (\(^13\)C NMR) ppm in CDCl\(_3\). The following abbreviations (or combinations thereof) were used to describe \(^1\)H NMR multiplicities: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad, app.– apparent. High resolution mass spectra (HRMS) were recorded on Bruker Daltonics microTOF-II or Waters QTOF XEVO-G2 spectrometer equipped with ESI ion source. IR spectra recorded on Perkin Elmer Spectrum BX FT-IR System. Optical rotations were obtained on a KRUSS P3001RS automatic digital polarimeter at 589 nm and \([\alpha]_20^\circ\) values are given in \(10^{-1}\) deg cm\(^{-1}\) g\(^{-1}\) and concentrations are given in units of g/100 cm\(^3\).

Abbreviations of chemicals: DCM - dichloromethane, DMPU -1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, EtOAc - ethylacetate, HMPA - Hexamethylphosphoramide, LHMDS - lithium bis(trimethylsilyl)amide, MeOH - methanol, PE - petrol ether (b.p. 40-60\(^\circ\)C fraction), TEA - triethylamine, TFA - trifluoroacetic acid, THF - tetrahydrofuran.
S1. Synthesis

Figure S1: Synthetic routes to target compounds.
Synthesis of 7

To a solution of LiHMDS (15.6 ml, 15.6 mmol, 1M, 2.5 eq.) in THF (60 ml) diketone 6 (1.59 g, 6.26 mmol, 1.0 eq.) in THF (20 ml) was added dropwise at -78°C. Some white precipitate of dienolate of 6 formed shortly after addition and the viscosity of the solution markedly increased. To complete enolization, the mixture was allowed to warm to -40°C and then cooled down to -78°C. HMPA (2.71 ml, 15.6 mmol, 2.5 eq.) was added followed by ethyl cyanoformate (1.54 ml, 15.6 mmol, 2.5 eq.). Reaction mixture was stirred for 15 min at -78°C and quenched by pouring cool reaction mixture into water. Crude product was extracted with DCM (3x10 ml), dried over Na₂SO₄ and concentrated under reduced pressure. Column chromatography on silica gel (35.0 g) eluting with EA/PE (1:50 - 1:30) gradient solvent system afforded 1.76 g (70%) of 7 as a colorless oil.

Note: HMPA can be replaced with less toxic DMPU with c.a. 10% reduction in yield.

[α]D = +20° (c 1.0 in CHCl₃)

**FTIR** (neat, cm⁻¹): 2981, 2933, 1701, 1662, 1284, 1208.

**¹H NMR** (400 MHz, CDCl₃/TFA) δ 1.30 (t, J = 7.2 Hz, 6Hz, CH₃), 1.46 (s, 9H), 2.55 (dd, J = 16.1 Hz, J = 7.3 Hz, 2H, CH₂), 2.67 (m, 2H, CH₂), 4.21 (q, J = 7.2 Hz, 4H, CH₂(Et)), 4.66 (d, J = 5.6 Hz, 1H, CH), 4.83 (d, J = 5.6 Hz, 1H, CH), 12.08 (s, 1H, OH), 12.14 (s, 1H, OH).

**¹³C NMR** (100 MHz, CDCl₃) δ 14.2, 26.3, 26.6, 28.3, 48.3, 49.9, 60.8, 80.9, 95.2, 95.7, 152.8, 169.0, 169.8, 171.9, 172.1.

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**HRMS** (ESI) calc. for C₁₉H₂₈NO₈ (M+H⁺): 398.1809, Found: 398.1814.
Synthesis of 10

To a solution of 7 (500 mg, 1.26 mmol, 1.0 eq.) in DCM (20 ml) was added TFA (5 ml, 50 eq.) dropwise. The mixture was stirred at rt for 3h and then evaporated to dryness. The solid residue was dissolved in dry DCM (20 ml) followed by the addition of 9 (1.78 g, 1.89 mmol, 1.5 eq.) (Scheme S1), triethylamine (0.27 ml, 1.89 mmol, 1.5 eq.) and NaBH(OAc)$_3$ (800 mg, 3.77 mmol, 3.0 eq.). The reaction mixture was stirred at rt for 3 days until TLC (EtOAc) shows full consumption of the deprotected 7 (FeCl$_3$ TLC stain). Reaction mixture was then evaporated to dryness and purified by column chromatography on silica gel (PE/EtOAc 35 : 1) to afford 1.25 g (81 %) of 10 as a yellowish solid.

$\left[\alpha\right]_D = +65^\circ$ (c 1.51 in CHCl$_3$)

**FTIR** (neat, cm$^{-1}$): 2924, 2854, 1660, 1596, 1207, 1164.

**$^1$H NMR** (400 MHz, CDCl$_3$/TFA) $\delta$ 12.03 (s, 2H, OH), 6.61 (d, $J = 2.2$ Hz, 2H, CH (arom.)), 6.55 (d, $J = 2.2$ Hz, 4H, CH (arom.)), 6.52 (t, $J = 2.2$ Hz, 1H, CH (arom.)), 6.4 (t, $J = 2.2$ Hz, 2H, CH (arom.)), 4.93 (s, 2H, CH$_2$ (benzylic)), 4.22 (q, $J = 7.1$ Hz, 4H, OCH$_2$), 3.93 (t, $J = 6.6$ Hz, 8H, CH$_2$), 3.64 (ABq, $\Delta \delta_{AB} = 0.08$, $J = 13.5$ Hz, 2H, CH (benzylic)), 3.43 (d, $J = 5.9$ Hz, 2H, CH), 2.64 (dd, $J = 16.0$ Hz, $J = 7.0$ Hz, 2H, CH$_2$), 2.41 (d, $J = 16$ Hz, 2H, CH$_2$), 1.76 (p, $J = 6.6$ Hz, 8H, CH$_2$), 1.18-1.50 (m, 60H, CH$_2$ and CH$_3$(Et)), 0.88 (t, $J = 6.6$ Hz, 12H, CH$_3$).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 1172.2, 170.5, 160.96, 160.5, 160.1, 140.2, 139.0, 107.6, 105.8, 101.0, 100.9, 94.8, 70.2, 68.1, 60.6, 56.0, 54.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 24.8, 22.7, 14.2, 14.1.

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**HRMS** (ESI) calc. for C$_{75}$H$_{118}$NO$_2$ (M+H$^+$): 1224.8649; Found: 1224.8654.
Synthesis of 2

A mixture of β-keto ester 10 (1.156 g, 0.92 mmol, 1.0 eq.), guanidine carbonate (442 mg, 4.61 mmol, 5.0 eq.) and K$_2$CO$_3$ (442 mg, 4.61 mmol, 5.0 eq.) in MeOH (20 ml) was heated under reflux overnight. Reaction mixture was cooled down, diluted with water and extracted with CH$_2$Cl$_2$ (3 x 5 ml). Combined organic phases were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Crude material was dissolved in minimum amount CHCl$_3$, precipitated with MeOH and filtered. Filter cake was washed with MeOH to afford 906 mg (81 %) of 2 as off-white powder.

[α]$_D$ = +15° (c 0.1 in CHCl$_3$)

mp (enantiopure) > 230 °C (decomp.), (rac) > 280 °C (decomp.)

FTIR (neat, cm$^{-1}$): 3329, 3152, 2924, 2853, 1654, 1596, 1458, 1166, 1054.

$^1$H NMR (400 MHz, CDCl$_3$/TFA) δ 11.14 (s, 2H, NH), 6.75 (s, 1H, CH (arom.)), 6.61 (s, 6H, CH (arom.)), 6.54 (s, 2H, CH (arom.)), 5.19 (br, 2H, CH$_2$), 4.49 (d, J =13.0 Hz, 1H, CH), 4.36 (d, J =13.0 Hz, 1H, CH), 4.03 (t, J =7.0 Hz, 8H, CH$_2$), 3.34 (d, J =18.0 Hz, 2H, CH$_2$), 3.12 (d, J =18.0 Hz, 2H, CH$_2$), 1.78 (t, J =7.0 Hz, 8H, CH$_2$), 1.16-1.50 (m, 56 H, CH$_2$), 1.87 (t, J =7.0 Hz, 12H, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.8, 162.3, 161.9, 161.5, 160.8, 160.2, 159.7, 152.1, 144.4, 138.1, 127.86, 118.5, 115.7, 112.9, 110.0, 107.5, 106.54, 104.3, 102.6, 70.5, 57.6, 51.5, 31.9, 29.6, 29.3, 28.9, 25.8, 22.7, 13.9.

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HRMS (ESI) calc. for C$_{73}$H$_{112}$N$_7$O$_8$ (M+H$^+$): 1214.8567; Found: 1214.8582.
Synthesis of 11

To a suspension of CuCN (301 mg, 3.36 mmol, 4.2 eq.) in dry THF (4.0 ml) vinyl magnesium solution (3.2 ml, 1.0 M in THF, 3.32 mmol, 4.15 eq.) was added dropwise at -20°C. The temperature was gradually raised to c.a. -10°C resulting in deep brown colour. The mixture was cooled to -78°C and a solution of bicyclo[3.3.1]nona-3,7-diene-2,6-dione 4 (0.21 g, 0.8 mmol) in dry THF (4.0 ml) was added dropwise. After 10 min, cooling bath was removed and the reaction mixture was quenched with 1.0 M HCl solution (15 mL). The mixture was extracted with EtOAc, combined organic phase was diluted with H₂O and filtered through CELITE. Organic phase was washed with NaHCO₃, dried over Na₂SO₄ and concentrated. The residue was purified by flash chromatography (PE/EtOAc 95:5) to afford 175 mg (64%) of 11 as a colourless solid.

\[ \alpha \] D = +103° (c 1.0 in CHCl₃)

FTIR (neat, cm⁻¹): 2955, 1645, 1603, 1442, 1210.

mp 81-82°C

1H NMR (400 MHz, CDCl₃) δ 12.49 (s, 2H, OH), 6.00-5.85 (m, 2H, C=CH), 5.15 (dt, \( J = 10.2 \) Hz, \( J = 1.2 \) Hz, 2H, C=CH₂), 5.01 (dt, \( J = 17.1 \) Hz, \( J = 1.2 \) Hz, 2H, C=CH₂), 3.73 (s, 6H, COOCH₃), 3.50 (app. d, \( J = 5.3 \) Hz, 2H, CH₂), 2.49-2.45 (m, 2H, CH), 1.79 (app. t, \( J = 3.0 \) Hz, 2H, CH₂).

13C NMR (100 MHz, CDCl₃) δ 174.1, 173.0, 139.8, 115.9, 97.7, 51.5, 40.7, 38.3, 17.5.

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HRMS (ESI) calc. for C₁₇H₂₁O₆ (M+H⁺): 321.1338; Found: 321.1331.
Synthesis of 12

A glass test tube was charged with 11 (386 mg, 1.20 mmol, 1.00 eq.), N-Boc-cysteamine (963 mg, 5.43 mmol, 4.50 eq.) and benzophenone (227 mg, 1.24 mmol, 1.03 eq.) under N₂. Dry THF (13 mL) was added and the solution was irradiated with UV lamp (365 nm, 8W) for 8 h. Then, solvent was removed under reduced pressure and the residue was purified by flash chromatography (PE/EtOAc 40 : 1 to 8: 1) to afford 677 mg (84%) of 12 as a colourless oil.

[α]D = +60.3° (c 1.16 in CHCl₃)

FTIR (neat, cm⁻¹): 3324, 2922, 2853, 1645, 1113.

¹H NMR (400 MHz, CDCl₃) δ 12.33 (s, 2H, OH), 5.01 (bt, 2H, NH), 3.77 (s, 6H, COOCH₃), 3.39-3.29 (m, 4H, N-CH₂), 2.78 (app.d, J = 9.8 Hz, 2H, CH), 2.68 (overlapping t, 6H, CH(H) and CH₂), 2.65-2.55 (m, 2H, CH(H)), 2.49 (br. s, 2H, CH), 2.01-1.89 (m, 2H, CH(H)), 1.83 (br. s, 2H, CH₂), 1.66-1.54 (m, 2H, CH(H)), 1.46 (s, 9H, Boc).

¹³C NMR (100 MHz, CDCl₃) δ 173.7, 172.8, 100.1, 79.4, 51.6, 39.7, 36.9, 36.0, 33.4, 32.3, 30.0, 28.4, 18.4.

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HRMS (ESI) calc. for C₃₁H₅₀N₂O₁₀S₂ (M+Na⁺): 697.2805, Found: 697.2817.
Synthesis of 14

Preparation of isocyanate 13. A mixture of acid X1 (315 mg, 0.57 mmol, 1.0 eq.), triethylamine (148 \( \mu l \), 1.04 mmol, 2.0 eq.) and diphenylphosphoryl azide (133 \( \mu l \), 0.61 mmol, 1.15 eq.) in dry toluene (7.0 ml) was heated at 40°C for 1.5 h. Then, the temperature was increased to 90°C and heating was continued for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was dried in high vacuum. The crude isocyanate 13 so-obtained was used in the next step without further purification.

Compound 12 (80 mg, 0.13 mmol, 1.0 eq.) was dissolved in dry DCM (5.0 ml) and TFA (0.5 ml) was added dropwise while cooling reaction mixture in an ice bath. After addition, the mixture was allowed to slowly reach the room temperature (without removing the ice bath). Then, the reaction mixture was stirred for an additional hour. The volatiles were removed under reduced pressure and the residue was dried under high vacuum. The crude salt obtained above was dissolved in THF (8.0 ml) followed by addition of triethylamine (0.2 ml). The solution obtained was added to isocyanate 13 (see the procedure above) and the mixture was heated at 50°C in a sealed vial overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (PE to DCM/MeOH 60 : 1) to afford 121 mg (62%) of 14 as a colourless oil.

FTIR (neat, cm\(^{-1}\)): 2923, 2854, 1606, 1504, 1225, 1203.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)
- 12.52 (s, 2H, OH),
- 6.78 (s, 2H, NH),
- 6.58 (s, 4H, CH (arom.)),
- 5.49 (t, \( J = 5.5 \) Hz, 2H, NH),
- 3.96-3.87 (m, 12H, -OCH\(_2\)),
- 3.76 (s, 6H, COOCH\(_3\)),
- 3.61-3.34 (m, 4H, CH\(_2\)),
- 3.96-3.87 (m, 12H, -OCH\(_2\)),
- 3.76 (s, 6H, COOCH\(_3\)),
- 3.61-3.34 (m, 4H, CH\(_2\)).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)
- 173.6, 172.9, 155.8, 153.4, 134.4, 134.1, 100.5, 99.8, 73.6, 69.1, 51.8, 39.28, 36.6, 35.9, 33.1, 32.3, 31.9, 30.3, 30.1, 29.8, 29.7, 29.5, 29.42, 29.38, 26.1, 22.7, 18.3, 18.4.
HRMS (ESI) calc. for C\textsubscript{95}H\textsubscript{164}N\textsubscript{4}O\textsubscript{10}S\textsubscript{2} (M+H\textsuperscript{+}): 1650.1764, Found: 1650.1772.
Synthesis of 3

A mixture of 14 (573 mg, 0.347 mmol, 1.0 eq.) and guanidinium carbonate (625 mg, 6.94 mmol, 20.0 eq.) in MeOH (15 ml) was heated at 80°C in a sealed vial overnight. The solvent was removed under reduced pressure and the residue was quenched with excess of 1.0 M HCl (aq.) solution. The water phase was extracted with Et₂O several times. The organic phase was washed with sat. NaHCO₃ solution and dried with Na₂SO₄. The solution was concentrated under reduced pressure and the residue was purified by flash chromatography (DCM/MeOH from 250 : 1 to 30 : 1) to afford 450 mg (80%) of 3 as a colourless glass.

FTIR (neat, cm⁻¹): 2922, 2853, 1644, 1603, 1503, 1226, 1113.

¹H NMR (400 MHz, CDCl₃/TFA) δ 6.46 (s, 4H, CH (arom.)), 4.03 (t, J =6.8 Hz, 4H, -OCH₂-), 3.94 (t, J =5.9 Hz, 8H, -OCH₂-), 3.49 (br.t, 2H, NH), 3.02 (br. s, 2H, CH₂), 2.92-2.80 (m, 4H, CH (H) and CH), 2.79-2.63 (m, 6H, CH (H) and CH₂), 2.10 (br. s, 2H, CH₂), 2.06-1.96 (m, 2H, CH (H)), 1.84-1.71 (m, 12H, CH₂), 1.71-1.57 (m, 2H, CH(H)), 1.50-1.39 (m, 12H, CH₂), 1.39-1.19 (m, 72H, CH₂), 0.95-0.84 (m, 18H, CH₃).

¹³C NMR (100 MHz, CDCl₃/TFA) δ 160.8, 159.1, 153.6, 151.9, 151.2, 135.4, 131.3, 113.0, 103.6, 74.7, 69.4, 39.5, 36.6, 32.7, 31.90, 31.87, 31.6, 29.8, 29.7, 29.61, 29.57, 29.55, 29.5, 29.3, 29.1, 26.0, 25.9, 22.7, 22.6, 14.1.

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HRMS (ESI) calc. for C₉₅H₁₆₂N₁₀O₁₀S₂ (M+H⁺): 1668.1990; Found: 1668.1995.
S2. Solid State NMR

All solid-state magic-angle spinning (MAS) NMR experiments were performed at either 20.0 (Bruker Avance III) or 14.1 (Bruker Avance II+) T, operating at a $^1$H Larmor frequency of 850 and 600 MHz, respectively. Experiments were performed using a 1.3 mm triple-resonance probe (operating in double-resonance mode), except for CP MAS experiments whereby a 3.2 or 4 mm probe was used. In all cases, the $^1$H $\pi/2$ pulse duration was 2.5 $\mu$s. Sign discrimination in the F1 dimension of 2D experiments was achieved using the States-TPPI (DQ/SQ MAS) or States methods. Note that, in 2D spectra, positive and negative contours are shown in black and red, respectively. For $^1$H – $^1$H DQ/SQ MAS experiments, a 16-step phase cycle was used to select $\Delta p = \pm 2$ on the DQ excitation pulses (4 steps) and $\Delta p = \pm 1$ (4 steps) on the z-filter /2 pulse, where p is the coherence order. For $^{14}$N – $^1$H HMQC experiments a 4-step nested phase cycle was used to select changes in coherence order $\Delta p = \pm 1$ (on the first $^1$H pulse, 2 steps) and $\Delta p = \pm 1$ (on the last $^{14}$N pulse, 2 steps).

In all experiments presented, $^1$H and $^{13}$C chemical shifts were referenced with respect to neat TMS using L-alanine as a secondary reference: 1.3 ppm for the CH$_3$ $^1$H resonance, corresponding to 1.85 ppm for adamantane, $^3$, and 20.5 ppm for the CH$_3$ $^{13}$C resonance, corresponding to 38.5 ppm for adamantane $^4$. $^{14}$N chemical shifts were referenced relative to neat CH$_3$NO$_2$ using the $^{14}$N resonance of NH$_4$Cl (powdered solid) at 341.2 ppm as an external reference $^5$. To convert to the chemical shift scale frequently used in protein NMR, where the alternative IUPAC reference (see Appendix 1 of ref $^6$) is liquid ammonia at 50 °C, it is necessary to add 379.5 ppm to the given values.$^7$. $^1$H, $^{13}$C, $^{14}$N and $^{15}$N shifts can be specified to an accuracy of ±0.2, ±0.1, ±5 and ±0.1 ppm, respectively.

$^1$H – $^1$H DQ/SQ MAS experiments.$^8$, $^9$ One rotor period of BABA recoupling$^{10}$, $^{11}$ was used for the excitation and reconversion of DQ coherence. For each of 256 $t_1$ FIDs, 16 transients were co-added with a recycle delay of 6 seconds. The $F_1 = 2F_2$ diagonal is indicated as a dashed black line. The base contour level is shown at 1% of the maximum peak intensity.

$^{14}$N – $^1$H HMQC experiments.$^9$, $^{12}$, $^{13}$ The spectrum was recorded using the R$^3$ recoupling scheme $^{14}$ for the recoupling of the $^{14}$N – $^1$H heteronuclear dipolar couplings for a $\tau_{R CPL} = 107$ $\mu$s. For each of 32 $t_1$ FIDs, 128 transients were co-added with a recycle delay of 6 seconds. The base contour level is shown at 26% of the maximum peak intensity.

$^1$H – $^{13}$C and $^1$H – $^{15}$N CP MAS experiments. Ramped CP$^{15}$ was employed for a contact time of 1 ms ($^1$H – $^{13}$C), 5 ms ($^1$H – $^{15}$N, enantiopure) or 2 ms ($^1$H – $^{15}$N, racemic). SPINAL-64 $^1$H decoupling$^{16}$ with a pulse length of 6.0 $\mu$s ($^1$H – $^{13}$C), 5.8 $\mu$s ($^1$H – $^{15}$N, enantiopure) or 4.8 $\mu$s ($^1$H – $^{15}$N, racemic) at a $^1$H nutation frequency of 100 kHz was applied during the acquisition of the FID. The $^1$H – $^{13}$C spectrum was recorded with 11264 co-added transients and a recycle delay of 6 seconds. The $^1$H – $^{15}$N spectra were recorded with 30720 (enantiopure) or 22528 (racemic) co-added transients and
a recycle delay of 3 seconds.
Table S1: DQ correlations extracted from the $^1$H – $^1$H DQ/SQ MAS spectrum of 1b (see Fig. 3)

| Entry | correlation | Sum of SQ freq. (ppm) | DQ freq. (ppm) |
|-------|-------------|-----------------------|----------------|
| 1     | CH$_3$-CH$_3$ | 0.9+0.9 | 1.8 |
| 2     | CH$_2$-CH$_2$ | 1.1+1.1 | 2.2 |
| 3     | CH$_2$-CH  | 1.1+2.8 | 3.9 |
| 4     | CH$_2$-H$_a$ | 1.1+7.4 | 8.5 |
| 5     | CH$_2$-H$_b$ | 1.1+10.3 | 10.4 |
| 6     | CH-H2  | 2.8+12.1 | 14.9 |
| 7     | H$_a$-H$_b$ | 7.4+10.3 | 17.7 |
| 8     | CH$_3$-H1 | 0.9+17.0 | 17.9 |
| 9     | H$_a$-H2 | 7.4+12.1 | 19.5 |
| 10    | H$_b$-H1 | 10.3+17.0 | 27.3 |

$^{14}$N chemical shifts

NH$_2$: -65 ppm
N – H2: -75 ppm
N – H1: -105 ppm
S2.2 Racemic vs chiral monomer

Compared to enantiopure 1b, racemic 1b is completely insoluble in chlorinated and aromatic solvents, indicating its different aggregation mode. Very similar $^1$H and $^{15}$N solid-state NMR spectra (see Figs. S2 and S3) were obtained for racemic 1b and enantiopure 1b, with slightly different chemical shift values (Table S2) and better resolution of Ha and Hb protons of the isocytosine amino group. The presence of two tautomeric forms of isocytosine in racemic 1b is easily explained assuming an energetically favourable 3H-bonding interaction of isocytosine units between two enantiomers that enable the formation of 1D zig-zag polymeric structures. These polymers can further assemble in orthogonal directions to form insoluble corrugated sheets (Fig. S4).

Figure S2: Two-dimensional solid state $^1$H – $^1$H DQ/SQ MAS (60 kHz MAS) spectrum of (a) enantiopure 1b (850 MHz) and (b) racemic 1b (600 MHz) with assignments. Characteristic through-space interactions are indicated with dashed lines.
Figure S3: $^1$H (600 MHz)-$^{15}$N CP MAS (10 kHz) spectra of (a) enantiopure 1b and (b) racemic 1b

Table S2: Single quantum (SQ) $^1$H chemical shifts for both the chiral monomer and racemic samples, extracted from the DQ/SQ MAS data. (Fig. S2)

| Site  | $\delta_{SQ}(^1\text{H})$/ppm | Site  | $\delta_{SQ}(^1\text{H})$/ppm |
|-------|-------------------------------|-------|-------------------------------|
| H1    | 16.9                          | H1    | 17.2                          |
| H2    | 11.9                          | H2    | 12.2                          |
| Hb'   | 10.6                          | Hb'   | 11.1                          |
| Hb    | 10.1                          | Hb    | 9.9                           |
| H'a   | 7.5                           | H'a   | 7.3                           |
| H'a   | 7.2                           | H'a   | 7.0                           |
| CH    | 2.7                           | CH    | 2.8                           |
| CH$_2$| 1.0                           | CH$_2$| 1.2                           |
| CH$_3$| 0.8                           | CH$_3$| 1.0                           |
Figure S4: Schematic representation of the formation of insoluble corrugated sheets via 2D 3H-heterochiral and 2H-homochiral bonding between the enantiomers of 1b. Solubilizing chains are omitted for clarity.
S3. Dynamic Light Scattering

Dynamic light scattering (DLS) experiments were carried out on a Zetasizer Nano Z (Malvern) instrument at 298K. Samples were prepared by dissolving the corresponding amount of monomers 1b-3 in toluene, filtering through PTFE membrane filter (AcroDisc, 0.12 micron) and aging for 24 hours. Measurements were at least duplicated and the data with good quality correlograms were used.

Figure S5: DLS data ($R_H$ – hydrodynamic radius) for monomers 1b (a), 2 (b) and 3 (c) in toluene solution. Concentrations and mean sizes of aggregates are indicated on the graphs. In case of monomer 3, bimodal distribution was observed, showing the presence of small amount of cyclic tetramers ($R_H$ 2-3 nm).

It should be noted that for compound 2, much smaller aggregates with $R_H < 10$ nm were obtained in chloroform solution as opposed to large polymeric assemblies in toluene (Fig. S6). This observation is in line with significantly weaker H-bonds in chlorinated solvents as compared to aromatic ones. Smaller degree of polymerization in this solvent was also evident from more resolved $^1H$ NMR spectrum as opposed to very broad spectrum in toluene (see Fig. S47).

Figure S6: Concentration dependence of hydrodynamic radii of (2$_4$)$_n$ aggregates in chloroform solution. Concentrations and mean sizes of aggregates are indicated on the graph.
S4. Viscosimetry

Viscosity was measured on AMVn Automated Micro Viscosimeter (Antor Paar) using 2.5 mm diameter gold coated ball at 298 K except for monomer 2, viscosity of which was probed at three different temperatures (298K, 338K and 258K). The corresponding solutions of monomers 2 and 3 were made in toluene, whereas chloroform was used for 1b due to solubility reasons.

Two distinct regimes can be identified in double logarithmic plot of 2 in toluene (Fig. S7). The low-slope regime can be attributed to a solution dominated by cyclic tetramers, whereas higher-slope dependence is caused by supramolecular polymerization of cyclic tetramers. In case of monomer 1b in chloroform, single-slope regime is observed, starting at very low concentration, which indicates very efficient supramolecular polymerization (Fig. S8).
High cooperativity of aggregation of monomer 1b in chloroform was demonstrated using viscosity measurements in the presence of simple isocytosine derivative ChS (Fig. S9), which might serve as a chain stopper for both tautomeric forms of the isocytosine. No change in viscosity was observed even in the presence of 10 mol % (solubility limit of ChS) of chain stopper.

Figure S9: Viscosity-concentration plot for 1b in chloroform (red) and in the presence of chain stopper (ChS) (blue).
S5. Preparation of Gels

Known amount of monomers 1b or 2 were added into 4.0 ml glass vial containing a stirring bar followed by solvent (methanol-free CHCl₃ or toluene). The vial was screw-capped with a plastic cap containing heat resistant PFET membrane. The vial was immersed into preheated oil bath (80°C for CHCl₃ and 100°C for toluene) and stirred until clear solution was obtained. The sol produced was cooled to ambient temperature and left undisturbed for 48 hr. The gelation concentration corresponds to the lowest concentration of monomer at which self-supporting gel is obtained. Gelation experiments in the presence of C₆₀/C₇₀ were done by adding known amount of toluene to a mixture of 4.0 equiv. of 1b or 2 and 1.0 equiv. C₆₀/C₇₀ (17.6 mg of 1b (19.00 mmol) and 5.6 mg C₆₀ (4.7 mmol) in 1.4 ml toluene; 9.3 mg of 1b (14.0 mmol) and 3.4 mg C₇₀ (3.5 mmol) in 1.0 ml toluene; 10.0 mg of 2 (8.2 mmol) and 1.5 mg C₆₀ (2.05 mmol) in 1.0 ml toluene). Heating of the mixture as above was continued until clear sol was obtained (Fig. S10). Significant increase of C₆₀ and C₇₀ solubility in toluene was observed.

Figure S10: Self-sustainable gels of C₆₀@(1b₄)ₙ in toluene (a), C₇₀@(1b₄)ₙ in toluene (b), (1b₄)ₙ (c) in toluene, (1b₄)ₙ in chloroform (d) and suspension of racemic (1b₄)ₙ and C₆₀ in toluene.
S6. Atomic Force Microscopy

AFM imaging was carried out in ambient conditions using the JPK NanoWizard 3 AFM in intermittent contact mode using the RTESPA (Bruker), Scout 350 (Nu Nano) and Tap300Al-G (Budget-Sensors) probes. The samples were prepared by drop casting the solution on the freshly cleaved muscovite mica and drying in nitrogen stream. The sample in manuscript Fig. 4a was dried 30s after drop casting. The sample in manuscript Fig. 4b was prepared by ultrasonicating the solution prior drop casting and drying in nitrogen stream after 10 s. Fibril structures were also observed in AFM images of (1b₄)ₙ and (3₄)ₙ from toluene solutions (Fig. S11).

Figure S11: AFM images (toluene solution) of (1b₄)ₙ (a-b), phase-contrast AFM image of (1b₄)ₙ (c) and (3₄)ₙ (d).

The AFM images of molecular tubes at lower concentrations suggest that the mica substrate has a templating effect on the fibrils. In case where individual fibrils are observed, the preferential alignment of fibrils along the mica crystallographic axes is seen. In case of entangled network of fibrils at higher concentration, the preferential angles seem to be determined by a combined action of surface templation and the fibril-fibril interaction, resulting in broader distribution of
preferred alignment angles. These preferences were revealed by applying histogram of oriented gradients [17] analysis (Fig. S12) on Fig. S13, with notable peaks at 63, 122, 55, 115 degrees. Large peaks at 0 and 90 degrees most likely result from the areas in the image where the fibrils are overlaid.

Figure S12: Histogram of oriented gradients analysis performed on AFM image in Fig.S13

Figure S13: Fibril network of entangled (1b₄)ₙ nanotubes obtained from chloroform solution on mica surface.
S7. Host-guest chemistry

The complexation of fullerenes by nanotubes \((1b_4)_n\) was assessed by using UV spectroscopy. The solid sample of the gels \(C_{60}(1b_4)_n\) and \(C_{70}(1b_4)_n\), prepared at 1:4 molar ratio, were diluted in toluene and UV spectra were collected (Fig. S14). Although only marginal shift of absorbance maximum (1-2 nm) was observed, the clear change in relative intensity of the absorption bands and the appearance of isobestic points was noted using both, \(C_{60}\) and \(C_{70}\). The very small change in absorbance maximum is in line with the results from our previous studies on fullerene complexation with structurally related tetrameric supramolecular host.\[^2\]

![Figure S14: Normalized UV spectra of \(C_{60}(1b_4)_n\) (a) and \(C_{70}(1b_4)_n\) (b) in toluene.](image)
S8. Molecular modelling

The geometry of tetramer $2_4$ was first calculated at semi-empirical level of theory (PM3, as implemented in Spartan 10) (Fig. S15). The optimized structure of tetramer $2_4$ was then used to construct an octameric fragment of the nanotube $(2_4)_n$. Due to the very large number of atoms, the resulting structure was optimized using molecular mechanics. The results of the molecular modelling show that despite the large size of solubilizing chains, a stable tubular polymer, potentially benefiting from favourable $\pi-\pi$ interactions, can form (Fig. S16).

Figure S15: a) Top-view of tetramer $2_4$. b) Minimalistic representation of tetramer $2_4$ without decyl chains with the diameter indicated (in Å). The solubilizing chains are labelled in magenta for clarity.

Figure S16: a) Top-view of octamer $(2_4)_2$. b) Side-view of octamer $(2_4)_2$. 
S9. Copies of NMR spectra
Figure S17: $^1$H NMR spectrum of 7.

return to Synthesis
Figure S18: $^{13}$C NMR spectrum of 7.

return to Synthesis
Figure S19: COSY NMR spectrum of 7.

return to Synthesis
Figure S20: HSQC NMR spectrum of 7.

return to Synthesis
Figure S21: $^1$H NMR spectrum of 10.

return to Synthesis
Figure S22: $^{13}$C NMR spectrum of 10.

return to Synthesis
Figure S23: COSY NMR spectrum of 10.
Figure S24: HSQC NMR spectrum of 10.

return to Synthesis
Figure S25: $^1$H NMR spectrum of 2.
Figure S26: $^{13}$C NMR spectrum of 2.

return to Synthesis
Figure S27: HSQC NMR spectrum of 2.

return to Synthesis
Figure S28: $^1$H NMR spectrum of 11.

return to Synthesis
Figure S29: $^{13}$C NMR spectrum of 11.

return to Synthesis
Figure S30: COSY NMR spectrum of 11.

return to Synthesis
Figure S31: HSQC NMR spectrum of 11.

return to Synthesis
Figure S32: $^1$H NMR spectrum of 12.

return to Synthesis
Figure S33: $^{13}$C NMR spectrum of 12.

return to Synthesis
Figure S34: COSY NMR spectrum of 12.

return to Synthesis
Figure S35: HSQC NMR spectrum of 12.
Figure S36: HMBC NMR spectrum of 12.

return to Synthesis
Figure S37: $^1$H NMR spectrum of 14.

return to Synthesis
Figure S38: $^{13}$C NMR spectrum of 14.

return to Synthesis
Figure S39: COSY NMR spectrum of 14.

return to Synthesis
Figure S40: HSQC NMR spectrum of 14.

return to Synthesis
Figure S41: HMBC NMR spectrum of 14.

return to Synthesis
Figure S42: $^1$H NMR spectrum of 3.
Figure S43. $^{13}$C NMR spectrum of 3.

return to Synthesis
Figure S44: COSY NMR spectrum of 3.

return to Synthesis
Figure S45: HSQC NMR spectrum of 3.

return to Synthesis
Figure S46: HMBC NMR spectrum of 3.
return to Synthesis
Figure S47: $^1$H NMR spectra of 1-3 in polymeric state
S9. References

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[18] Spartan'10, *Wavefunction Inc. 18401 Von Karman Avenue Suite 370. Irvine CA 92612 U.S.A.*