Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Formation of triple helical nanofibers using self-assembling chiral benzene-1,3,5-tricarboxamides and reversal of the nanostructure's handedness using mirror image building blocks

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Synthesis of benzene-1,3,5-tricarboxamides:

Compound 1: A 2.1 g (10 mmol) sample of benzene-1,3,5-tricarboxylic acid was dissolved in a mixture of 20 mL of N,N-dimethylformamide (DMF) in an ice-water bath. H-Val-OMe was isolated from 10.05 g (60 mmol) of the corresponding methyl ester hydrochloride by neutralization with saturated sodium carbonate, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 7.00 g (34 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DMF was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 X 50 mL), brine, 1 M sodium carbonate (3 X 50 mL), and brine (2 X 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield 4.2 g (76%). Anal. calcd for $C_{27}H_{39}N_3O_9$ (549.7): C, 59.00; H, 7.15; N, 7.65%; found: C, 59.02; H, 6.91; N, 7.84%; HRMS *m/z* (%): 550.0077 (100) $[M]^+$, 551.0021(40) $[M+H]^+$; ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 0.92-0.99 (m, 18H), 2.1-2.2 (q, 3H), 3.6 (s, 9H), 4.2-4.3 (t, *J* = 6 Hz, 3H), 8.4 (s, 3H), 8.96-8.99 (d, *J* = 9 Hz, 3H); $[\alpha]_D^{20}$ -35.0 (*c* 0.55, CH_3OH); IR (KBr) 1511 (NH bend), 1642 (C=O stretch), 1751 (ester C=O stretch), 3032 (NH stretch), 3257 cm^{-1} (NH stretch).

Compound 2: A 2.1 g (10 mmol) sample of benzene-1,3,5-tricarboxylic acid was dissolved in a mixture of 20 mL of N,N-dimethylformamide (DMF) in an ice-water bath. H-Leu-OMe was isolated from 10.9 g (60 mmol) of the corresponding methyl ester hydrochloride by neutralization with saturated sodium carbonate, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 7.0 g (34 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DMF was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 X 50 mL), brine, 1 M sodium carbonate (3 X 50 mL), and brine (2 X 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield 4.4 g (74%). Anal. calcd for $C_{30}H_{45}N_3O_9$ (591.7): C, 60.90; H, 7.67; N, 7.10%; found: C, 60.71; H, 7.73; N, 7.23%; HRMS *m/z* (%): 592.1215 (100) $[M]^+$, 593.1400 (35) $[M+H]^+$; ^1H NMR (300 MHz, $(CD_3)SO$) δ 0.87-0.93 (m, 18H), 1.54-1.60 (m, 3H), 1.7-1.8 (m, 6H), 3.6 (s, 9H), 4.05-4.1 (m, 3H), 8.4 (s, 3H), 9.07-9.09 (d, *J* = 6 Hz, 3H); $[\alpha]_D^{20}$ -28.0 (*c* 0.75, CH_3OH); IR (KBr) 1550 (NH bend), 1642 (amide C = O stretch), 1751 (ester C = O stretch), 3038 (NH stretch), 3263 cm^{-1} (NH stretch).

Compound 3: A 2.1 g (10 mmol) sample of benzene-1,3,5-tricarboxylic acid was dissolved in a mixture of 20 mL of N,N-dimethylformamide (DMF) in an ice-water bath. H-D-Val-OMe was isolated from 10.05 g (60 mmol) of the corresponding methyl ester hydrochloride by neutralization with saturated sodium carbonate, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 7.0 g (34 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DMF was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 X 50 mL), brine, 1 M sodium carbonate (3 X 50 mL), and brine (2 x50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield 4.1 g (73%). Anal. calcd for $C_{27}H_{39}N_3O_9$ (549.7): C, 59.00; H, 7.15; N, 7.65%; found: C, 59.02; H, 7.11; N, 7.42%; HRMS *m/z* (%): 550.0077 (100) $[M]^+$, 551.0021 (40) $[M+H]^+$; ^1H NMR (300 MHz, $(CD_3)_2SO$) δ 0.94-0.99 (m, 18H), 2.1-2.2 (q, 3H), 3.6 (s, 9H), 4.2-4.3 (t, *J* = 6 Hz, 3H), 8.4 (s, 3H), 8.96-8.99 (d, *J* = 9 Hz, 3H); $[\alpha]_D^{20}$ +35.0 (*c* 0.55, CH_3OH); IR (KBr) 1550 (NH bend), 1642 (amide C = O stretch), 1751 (ester C = O stretch), 3063 (NH stretch), 3238 cm^{-1} (NH stretch).

Compound 4: A 2.1 g (10 mmol) sample of benzene-1,3,5-tricarboxylic acid was dissolved in a mixture of 20 mL of N,N-dimethylformamide (DMF) in an ice-water bath. H-Aib-OMe (Aib = α-aminoisobutyric acid) was isolated from 9.2 g (60 mmol) of the corresponding methyl ester hydrochloride by neutralization with saturated sodium carbonate, subsequent extraction with ethyl acetate, and concentration (10 mL), and this was added to the reaction mixture, followed immediately by 7.00 g (34 mmol) of dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 h. DMF was evaporated, and the residue was taken in ethyl acetate (60 mL); dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 X 50 mL), brine, 1 M sodium carbonate (3 X 50 mL), and brine (2 X 50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield 4.3 g (84%). Anal. calcd for $C_{24}H_{33}N_3O_9$ (507.7): C, 56.80; H, 6.55; N, 8.28%; found: C, 56.52; H, 6.43; N, 8.31%; HRMS *m/z* (%) 508.0033 (100) $[M+H]^+$, 530.9799 (55) $[M+Na]^+$; ^1H NMR (300 MHz, $(CD_3)_2SO$) δ 1.47 (s, 18H), 3.5 (s, 9H), 8.4 (s, 3H), 8.9 (s, 3H); $[\alpha]_D^{20}$ 0.0 (*c* 0.8, CH_3OH); IR (KBr) 1553 (NH bend), 1644 (amide C=O stretch), 1743 (ester C=O stretch), 3059 (NH stretch), 3224 cm^{-1} (NH stretch).

Transmission Electron Microscopic studies: Transmission electron microscopy (TEM) measurements were carried out to observe finer morphological details. Transmission electron microscopic studies of benzene-1,3,5-tricarboxamides were carried out using methanol-water solution (1:1) of the corresponding compound (3 mg in 1 mL) on carbon-coated copper grid (300 mesh) by slow evaporation and vacuum drying at 30°C for two days. Images were taken at an accelerating voltage of 200 kV. TEM was performed using a JEM-2010 electron microscope. In a fresh experiment 3 mg of compound **1** is dissolved in 1 mL of methanol-water solution (1:1) with continuous sonication (TELSONIC (TEC15, moden No. 900818), 33 kHz, power 70 W) for 3 minutes and TEM measurements was prepared by evaporating the solution on carbon-coated copper grid (300 mesh) by slow evaporation.

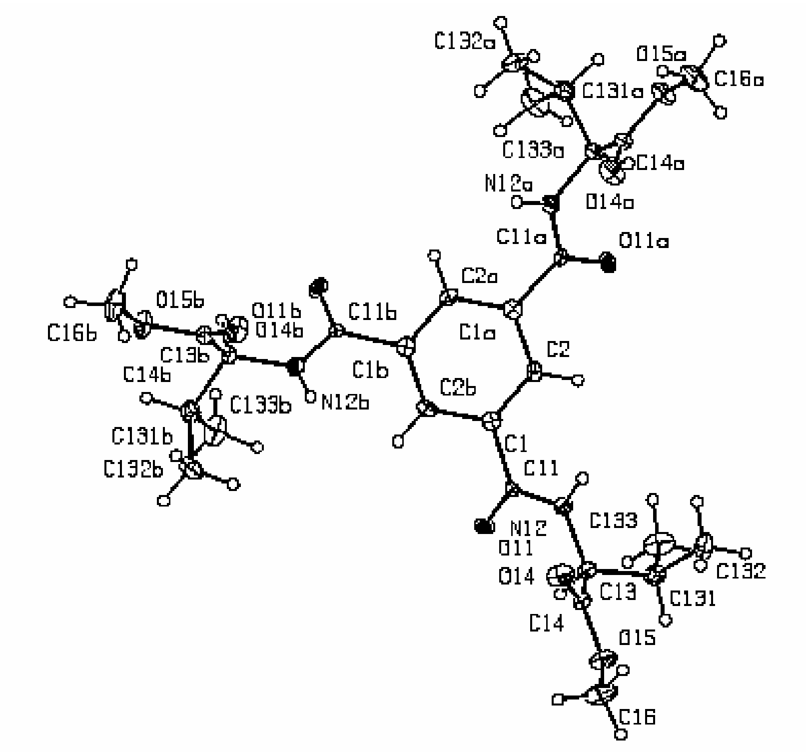


Figure S1: ORTEP diagram of compound **1** showing the atomic numbering scheme. Thermal ellipsoids are at a level of 30% probability. Symmetry elements are a: 2-y, 1+x-y, z and b: 1-x+y, 2-x, z.

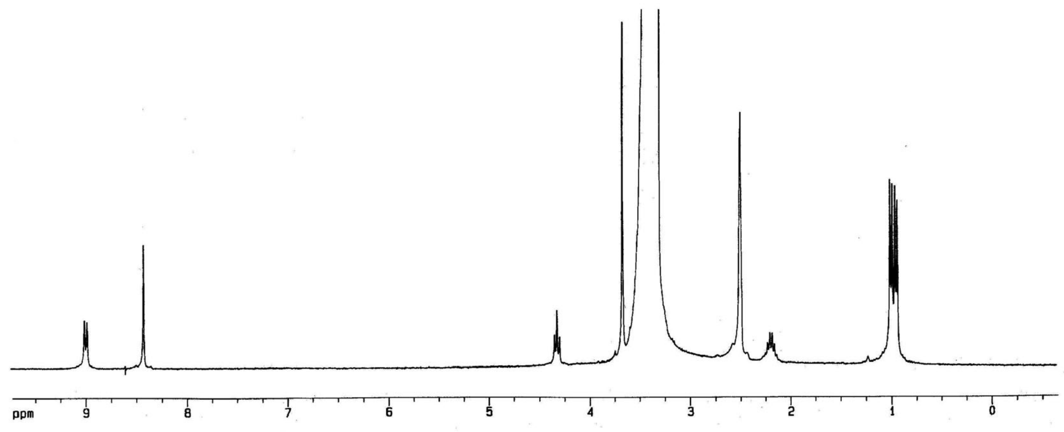


Figure S2: ^{1}H NMR spectra of compound **1** in $(CD_3)_2SO$.

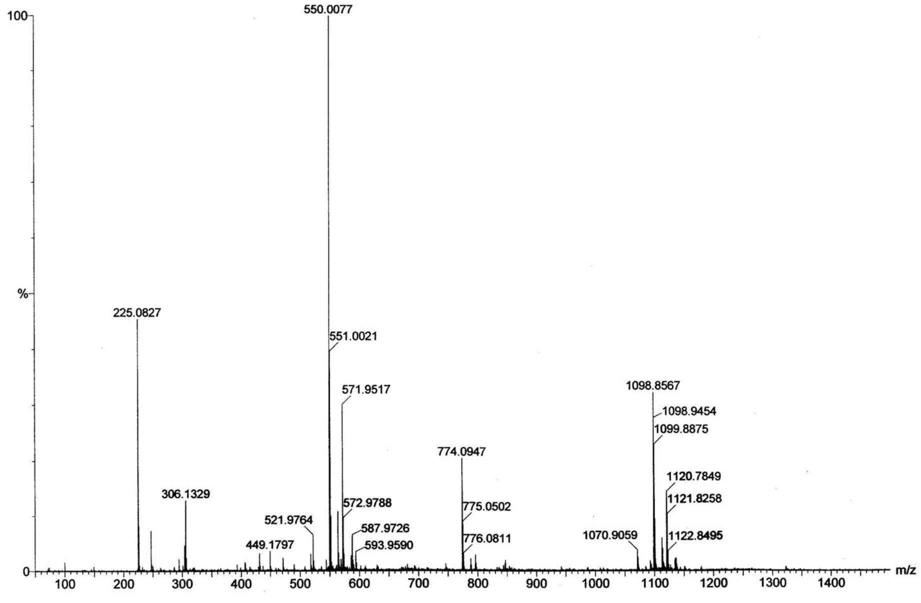


Figure S3: HRMS spectra of compound **1**.

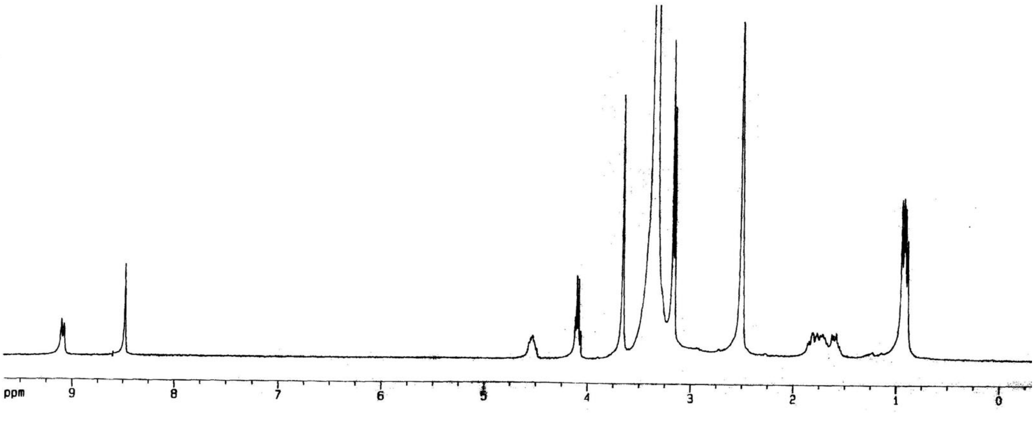


Figure S4: ^{1}H NMR spectra of compound **2** in $(CD_3)_2SO$.

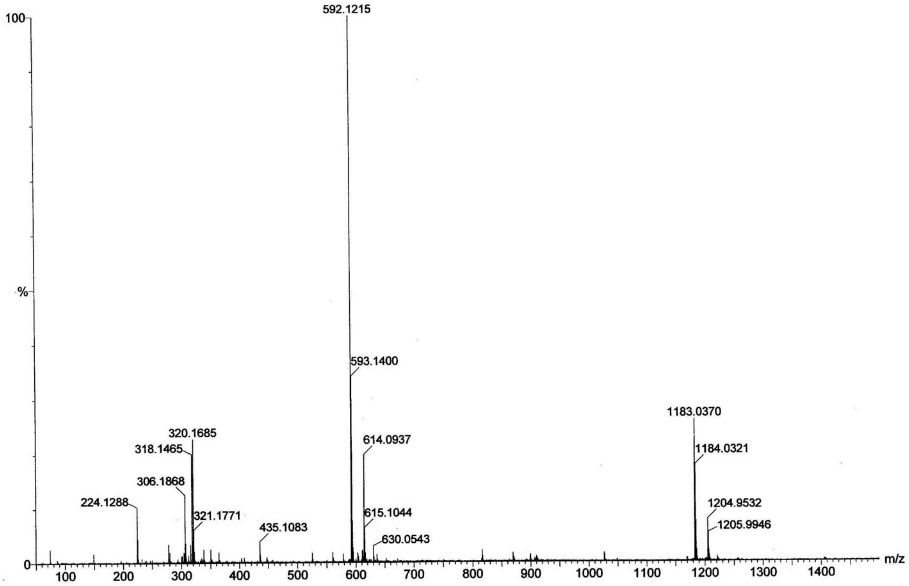


Figure S5: HRMS spectra of compound **2**.

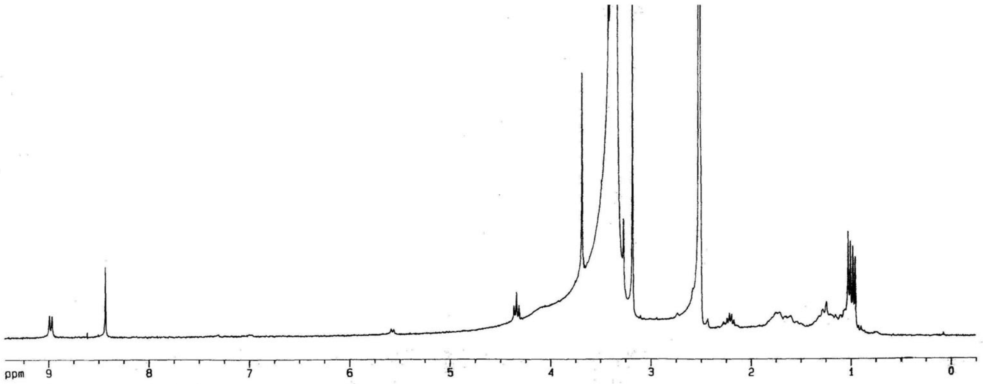


Figure S6: ^{1}H NMR spectra of compound **3** in $(CD_3)_2SO$.

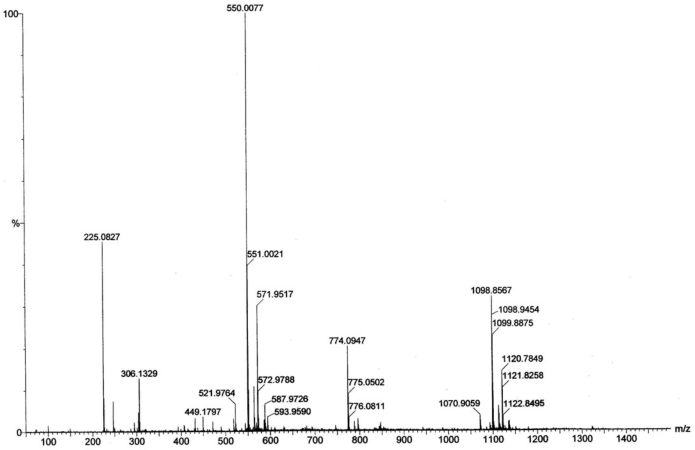


Figure S7: HRMS spectra of compound **3**.

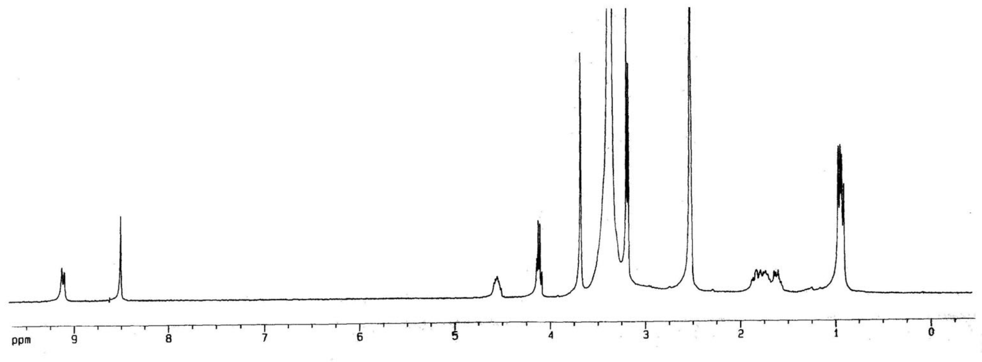


Figure S8: ^{1}H NMR spectra of compound **4** in $(CD_3)_2SO$.

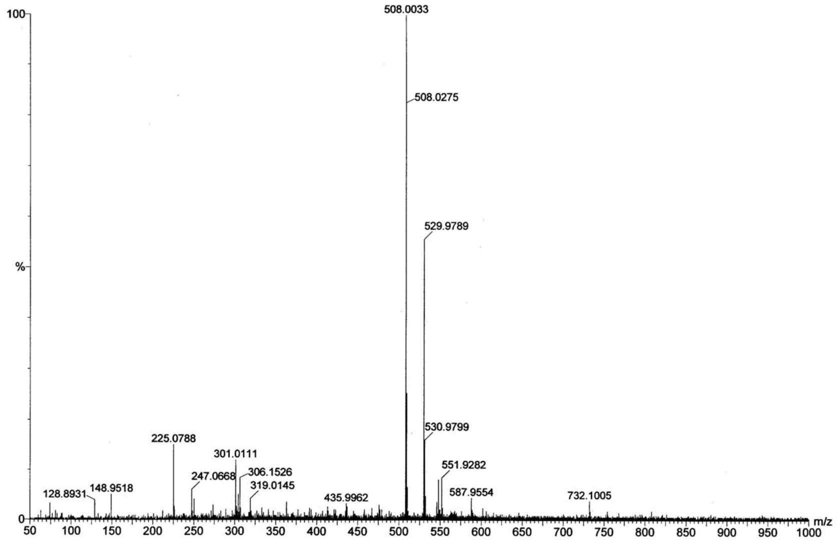


Figure S9: HRMS spectra of compound **4**.

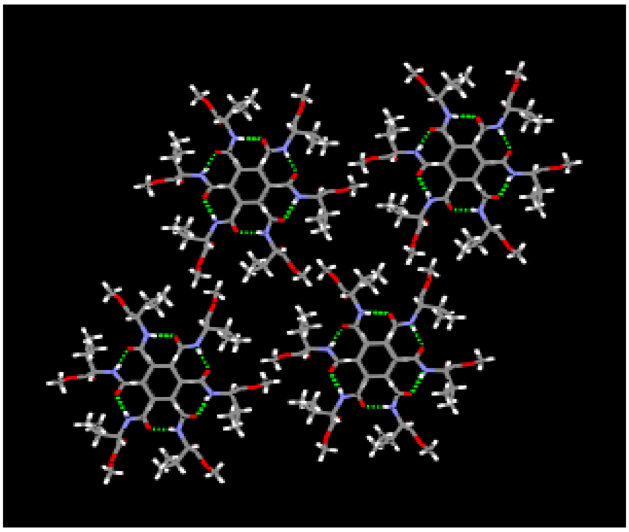
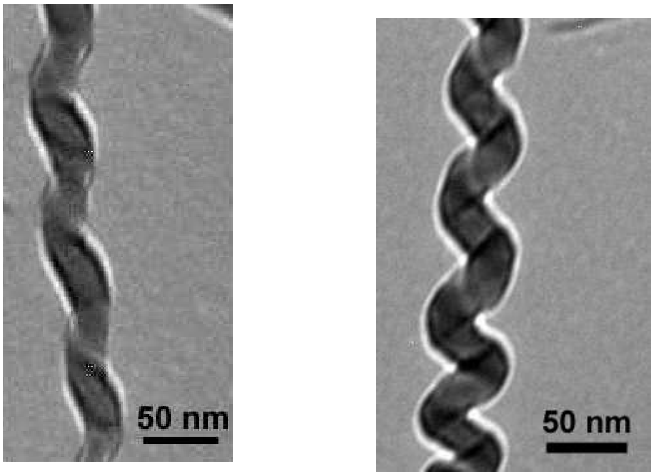
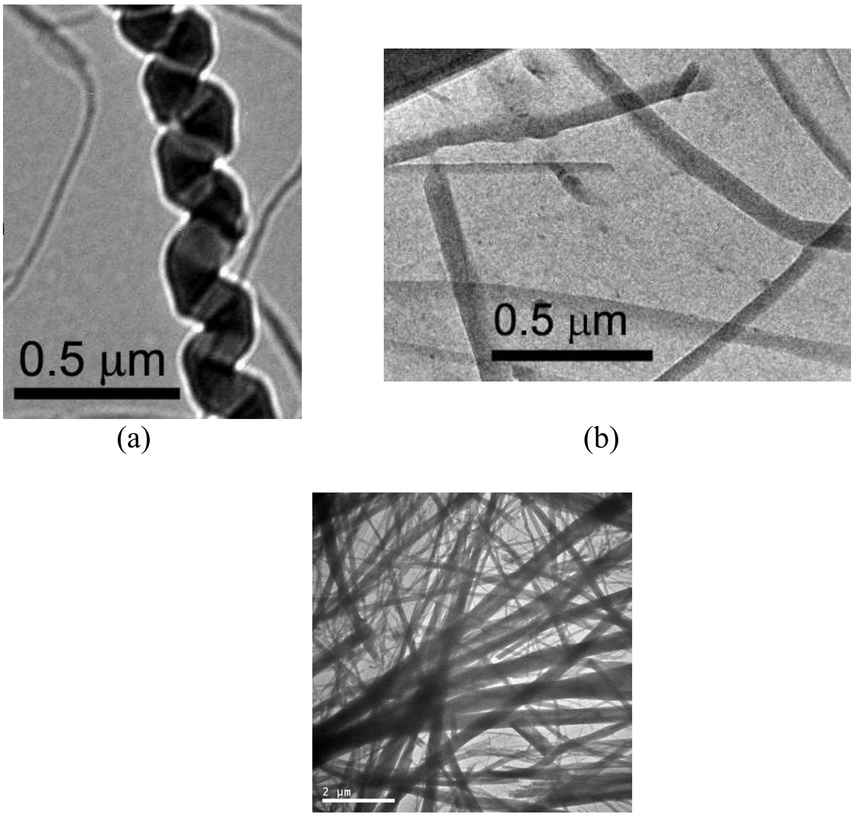


Figure S10: View down the supramolecular triple helix axis indicating higher ordered supramolecular arrays of interacting individual triple helical columns of compound **1** via non-hydrogen bonding non-covalent interactions.



(a) (b)

Figure S11: (a) Transmission electron microscopic (TEM) image of compound **1** upon sonication shows single stranded handed helical nanofiber with an average diameter of 40 nm. (b) TEM image of compound **3** upon sonication shows single stranded reversed handed helical nanofiber to that of compound **1** with an average diameter of 30 nm. Compounds **1** and **3** are enantiomers and it appeared that the chirality of the helical nanofibers is reversed when the mirror-imaged compound is used.



(a) (b)

(c)

Figure S12: (a) Transmission electron microscopic (TEM) image of compound **3** giving helical tape structures of width 175-195 nm at the concentration of 3.8 mg/mL in methanol-water solution (1:1). (b) TEM image of compound **1** shows narrower nanofibers of width 60-90 nm at the concentration of 2 mg/mL in methanol-water (1:1) solution. (c) TEM image of compound **1** giving nanofiber (diameter ≥ 180 nm) at the concentration of 3 mg/mL in dimethyl sulphoxide-water (1:1) solution.

Table S1. Selected torsion angles (°) of compound **1**.

Compound **1**	
C1-C11-N12-C13	-179.5(5)
C11-N12-C13-C14	-116.8(6)
N12-C13-C14-O15	179.9(5)

Table S2. Intermolecular hydrogen bonding parameters of compound **1**.

Compound	D-H···A	H···A/Å	D···A/Å	D-H···A/°	Symmetry
1	N12-H…O11	2.06	2.901(7)	164	1+x-y, x, 1/2+z