Supporting Information

Self-Assembly of Chiral Hexacatenar-Bisamides into a Columnar Structure

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1. General

All the starting materials were obtained from Aldrich or Lancaster Companies and used as received. Solvents were purified and dried by standard methods prior to use. The identification of the mesophases and the transition temperatures of the compounds were initially determined using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). The transition temperatures and associated enthalpies were determined by differential scanning calorimetry (Perkin Elmer DSC7). The absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV-Vis spectrometer. IR spectra were recorded using Perkin Elmer Spectrum 1000 FT-IR spectrometer. Mass spectra were recorded on a Jeol-JMS-600H spectrometer in FAB+ mode using 3-nitrobenzyl alcohol as a liquid matrix. CD spectra and specific rotation values were recorded with the aid of Jasco J-810 spectropolorimeter. Elemental analyses were done using Eurovector model EA 3000 CHNS analyzer. ^{1}H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz) spectrometer and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. X-ray diffraction studies were carried out on powder samples in Lindemann capillaries with CuK_α radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics.

2. Syntheses and Analytical data

General procedure for the synthesis of hexacatenar bisamides (HBA-1 to HBA-10).

To a clear solution of 3,4,5-trialkoxybenzoic acid **(1a / 1b)**[1a] (0.17 mmol, 1 equiv.) in dry THF (10 ml), DIEA (0.19 mmol, 1.1 equiv.) and HBTU (0.19 mmol, 1.1 equiv.) were added. To this reaction mixture, a solution of amines (**2** to **7**)[1].(0.17 mmol, 1 equiv.) in dry THF (10 ml) added and stirred at room temperature for 10 h under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 (25 ml), washed successively twice with 5% HCl, 5% aq $NaHCO_3$, brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to get the crude material which was

purified by column chromatography using neutral alumina. The column was eluted with 5 % EtOAc-hexanes to obtain a solid which was further purified by recrystallization from ethanol.

HBA-1: 3,4,5-Tris-decyloxy-*N*-[1(*S*)-(3,4,5-tris-decyloxy-phenylcarbamoyl)-ethyl]-benzamide. R_f = 0.60 in 20% EtOAc-hexanes; a gummy substance; yield: 64 %; IR (KBr pellet): ν_{max} in cm^{-1} 3290, 2918, 2848, 1690, 1650, 1560, 1121; $[\alpha]_D^{30}$ -7.01 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 263.91 nm, $\in$ = 1.04 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.50 (s, 1H, NH), 6.95 (s, 2H, Ar), 6.80 (s, 2H, Ar), 6.59 (d, *J* = 7.5 Hz, 1H, NH), 4.89 (m, 1H, CH), 4.02 – 3.87 (m, 12H, 6 × OCH_2), 1.88 – 0.86 (m, 117H, 7 × CH_3, 48 × CH_2); MS (FAB+): m/z calcd for $C_{76}H_{137}N_2O_8$ (M+1): 1206.9. Found: 1206.5; Anal. calcd for $C_{76}H_{136}N_2O_8$: C, 75.69; H, 11.37; N, 2.32. Found: C, 75.60; H, 11.46; N, 2.43.

HBA-2: 3,4,5-Tris-decyloxy-*N*-[3-methyl-1(*S*)-(3,4,5-tris-decyloxy-penylcarbamoyl)-butyl]-benzamide. R_f = 0.62 in 20% EtOAc-hexanes; a colorless solid; yield: 62 %; IR (KBr pellet): ν_{max} in cm^{-1} 3284, 2918, 2848, 1694, 1650, 1540, 1120; $[\alpha]_D^{30}$ -13.96 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 247.19 nm, $\in$ = 2.36 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.19 (s, 1H, NH), 6.95 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.38 (d, *J* = 7.2 Hz, 1H, NH), 4.74 (m, 1H, CH), 4.02 – 3.87 (m, 12H, 6 × OCH_2), 1.97 – 0.86 (m, 123H, 8 × CH_3, 49 × CH_2, 1 × CH); MS (FAB+): m/z calcd for $C_{79}H_{142}N_2O_8$: 1247.1. Found: 1247.9; Anal. calcd for $C_{79}H_{142}N_2O_8$: C, 76.03; H, 11.47; N, 2.25. Found: C, 75.89; H, 11.47; N, 2.43.

HBA-3: 3,4,5-Tris-decyloxy-*N*-[3-methyl-1(*R*)-(3,4,5-tris-decyloxy-phenylcarbamoyl)-butyl]-benzamide**.** R_f = 0.62 in 20% EtOAc-hexanes; a colorless solid; yield: 62%; IR (KBr pellet): ν_{max} in cm^{-1} 3286, 2920, 2858, 1690, 1640, 1536, 1128; $[\alpha]_D^{30}$ +14.23 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 263.81 nm, $\in$ = 6.28 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.23 (s, 1H, NH), 6.95 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.39 (d, *J* = 7.1 Hz, 1H, NH), 4.76 (m, 1H, CH), 4.01 – 3.87 (m, 12H, 6 × OCH_2), 1.99 – 0.86 (m, 123H, 8 × CH_3, 49 × CH_2, 1 × CH); MS (FAB+): m/z calcd for $C_{79}H_{143}N_2O_8$ (M+1): 1248.1. Found: 1248.5; Anal. calcd for $C_{79}H_{142}N_2O_8$: C, 76.03; H, 11.47; N, 2.25. Found: C, 75.96; H, 11.49; N, 2.36.

HBA-4: 3,4,5-Tris-decyloxy-*N*-[2-methyl-1(*S*)-(3,4,5-tris-decyloxy-phenylcarbamoyl)-propyl]-benzamide. R_f = 0.61 in 20% EtOAc-hexanes; a colorless solid; yield: 60 %; IR (KBr pellet): ν_{max} in cm^{-1} 3285, 2925, 2860, 1694, 1642, 1538, 1124; $[\alpha]_D^{29}$ -14.11 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 263.94 nm, $\in$ = 2.14 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.86 (s, 1H, NH), 6.97 (s, 2H, Ar), 6.79 (s, 2H, Ar), 6.39 (d, *J* = 8.6 Hz, 1H, NH), 4.45 (m, 1H, CH), 3.99 – 3.87 (m, 12H, 6 × OCH_2), 2.32 (m, 1H, 1 × CH), 1.82 – 0.86 (m, 120H, 8 × CH_3, 48 × CH_2); MS (FAB+): m/z calcd for $C_{78}H_{141}N_2O_8$ (M+1): 1234.1. Found: 1234.5; Anal. calcd for $C_{78}H_{140}N_2O_8$: C, 75.92; H, 11.44; N, 2.27. Found: C, 75.62; H, 11.65; N, 2.52.

HBA-5: 3,4,5-Tris-decyloxy-*N*-[2-methyl-1(*R*)-(3,4,5-tris-decyloxy-phenylcarbamoyl)-propyl]-benzamide. R_f = 0.61 in 20% EtOAc-hexanes; a colorless solid; yield: 61 %; IR (KBr pellet): ν_{max} in cm^{-1} 3283, 2929, 2868, 1690, 1640, 1540, 1125; $[\alpha]_D^{29}$ +16.02 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 263.90 nm, $\in$ = 2.00 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.93 (s, 1H, NH), 6.98 (s, 2H, Ar), 6.79 (s, 2H, Ar), 6.65 (d, *J* = 8.6 Hz, 1H, NH), 4.47 (m, 1H, CH), 4.01– 3.87 (m, 12H, 6 × OCH_2), 2.31 (m, 1H, 1 × CH), 1.82 – 0.86 (m, 120H, 8 × CH_3, 48 × CH_2); MS (FAB+): m/z calcd for $C_{78}H_{140}N_2O_8$: 1233.1. Found: 1233.9; Anal. calcd for $C_{78}H_{140}N_2O_8$: C, 75.92; H, 11.44; N, 2.27. Found: C, 75.86; H, 11.58; N, 2.44.

HBA-6: 3,4,5-Tris-dodecyloxy-*N*-[1(*S*)-(3,4,5-tris-dodecyloxy-phenylcarbamoyl)-ethyl]-benzamide. R_f = 0.61 in 20% EtOAc-hexanes; a colorless solid; yield: 63 %; IR (KBr pellet): ν_{max} in cm^{-1} 3287, 2919, 2849, 1697, 1602, 1558, 1121; $[\alpha]_D^{26}$ -10.03 (c = 1%, $CHCl_3$); UV–

Vis: λ_{max} = 247.87 nm, $\in$ = 1.58 × 10^3 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.39 (s, 1H, NH), 6.96 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.52 (d, *J* = 7.3 Hz, 1H, NH), 4.81 (m, 1H, CH), 4.01 – 3.87 (m, 12H, 6 × OCH_2), 1.82 – 0.86 (m, 141H, 7 × CH_3, 60 × CH_2); MS (FAB+): m/z calcd for $C_{88}H_{161}N_2O_8$ (M+1): 1374.2. Found: 1374.6; Anal. calcd for $C_{88}H_{160}N_2O_8$: C, 76.91; H, 11.74; N, 2.04. Found: C, 77.07; H, 12.04; N, 2.11.

HBA-7: 3,4,5-Tris-dodecyloxy-*N*-[3-methyl-1(*S*)-(3,4,5-tris-dodecyloxy-phenylcarbamoyl)-butyl]-benzamide. R_f = 0.61 in 20% EtOAc-hexanes; a colorless solid; yield: 60 %; IR (KBr pellet): ν_{max} in cm^{-1} 3266, 2920, 2849, 1669, 1628, 1540, 1117; $[\alpha]_D^{26}$ -13.05 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 264.94 nm, $\in$ = 2.23 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.30 (s, 1H, NH), 6.95 (s, 2H, Ar), 6.80 (s, 2H, Ar), 6.44 (d, *J* = 7.9 Hz, 1H, NH), 4.75 (m, 1H, CH), 4.00 – 3.85 (m, 12H, 6 × OCH_2), 1.93 – 0.86 (m, 147H, 8 × CH_3, 61 × CH_2, 1 × CH); ^{13}C NMR (100MHz, $CDCl_3$): 170.15, 167.50, 165.9, 153.16, 134.83, 133.34, 128.14, 105.75, 98.75, 73.48, 69.38, 68.97, 53.15, 40.71, 31.91, 30.31, 29.67, 29.37, 26.08, 24.95, 22.84, 22.67, 22.41, 14.07; MS (FAB+): m/z calcd for $C_{91}H_{167}N_2O_8$ (M+1): 1416.2. Found: 1416.1; Anal. calcd for $C_{91}H_{166}N_2O_8$: C, 77.17; H, 11.81; N, 1.98. Found: C, 76.98; H, 12.01; N, 2.27.

HBA-8: 3,4,5-Tris-dodecyloxy-*N*-[3-methyl-1(*R*)-(3,4,5-tris-dodecyloxy-phenylcarbamoyl)-butyl]-benzamide. R_f = 0.61 in 20% EtOAc-hexanes; a colorless solid; yield: 62 %; IR (KBr pellet): ν_{max} in cm^{-1} 3266, 2920, 2849, 1669, 1628, 1540, 1117; $[\alpha]_D^{26}$ +14.86 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 264.88 nm, $\in$ = 2.11 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.12 (s, 1H, NH), 6.95 (s, 2H, Ar), 6.80 (s, 2H, Ar), 6.43 (d, *J* = 7.9 Hz, 1H, NH), 4.75 (m, 1H, CH), 4.00 – 3.88 (m, 12H, 6 × OCH_2), 1.93 – 0.86 (m, 147H, 8 × CH_3, 61 × CH_2, 1 × CH); MS (FAB+): m/z calcd for $C_{91}H_{166}N_2O_8$: 1415.2. Found: 1415.7; Anal. calcd for $C_{91}H_{166}N_2O_8$: C, 77.17; H, 11.81; N, 1.98. Found: C, 76.98; H, 12.01; N, 2.25.

HBA-9: 3,4,5-Tris-dodecyloxy-*N*-[2-methyl-1(*S*)-(3,4,5-tris-dodecyloxy-phenylcarbamoyl)-propyl]-benzamide. R_f = 0.62 in 20% EtOAc-hexanes; a colorless solid; yield: 64 %; IR (KBr pellet): ν_{max} in cm^{-1} 3287, 2920, 2849, 1697, 1602, 1535, 1120; $[\alpha]_D^{26}$ -10.36 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 247.57 nm, $\in$ = 2.28 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.07 (s, 1H, NH), 6.97 (s, 2H, Ar), 6.79 (s, 2H, Ar), 6.69 (d, *J* = 8.7 Hz, 1H, NH), 4.53 (m, 1H, CH), 3.99 – 3.86 (m, 12H, 6 × OCH_2), 2.34 (m, 1H, 1 × CH), 1.81 – 0.86 (m, 144H, 8 × CH_3, 60 × CH_2); MS (FAB+): m/z calcd for $C_{90}H_{164}N_2O_8$: 1401.2. Found: 1401.1; Anal. calcd for $C_{90}H_{164}N_2O_8$: C, 77.07; H, 11.79; N, 2.00. Found: C, 77.29; H, 11.95; N, 2.19.

HBA-10: 3,4,5-Tris-dodecyloxy-*N*-[2-methyl-1(*R*)-(3,4,5-tris-dodecyloxy-phenylcarbamoyl)-propyl]-benzamide. R_f = 0.62 in 20% EtOAc-hexanes; a colorless solid; yield: 65 %; IR (KBr pellet): ν_{max} in cm^{-1} 3289, 2921, 2849, 1697, 1602, 1534, 1121; $[\alpha]_D^{26}$ +9.96 (c = 1%, $CHCl_3$); UV–Vis: λ_{max} = 247.83 nm, $\in$ = 2.33 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.92 (s, 1H, NH), 6.97 (s, 2H, Ar), 6.79 (s, 2H, Ar), 6.65 (d, *J* = 8.5 Hz, 1H, NH), 4.48 (m, 1H, CH), 3.99 – 3.87 (m, 12H, 6 × OCH_2), 2.34 (m, 1H, 1 × CH), 1.81 – 0.85 (m, 144H, 8 × CH_3, 60 × CH_2); MS (FAB+): m/z calcd for $C_{90}H_{164}N_2O_8$: 1401.2. Found: 1401.1; Anal. calcd for $C_{90}H_{164}N_2O_8$: C, 77.07; H, 11.79; N, 2.00. Found: C, 77.37; H, 11.59; N, 2.10.

3. Additional datas

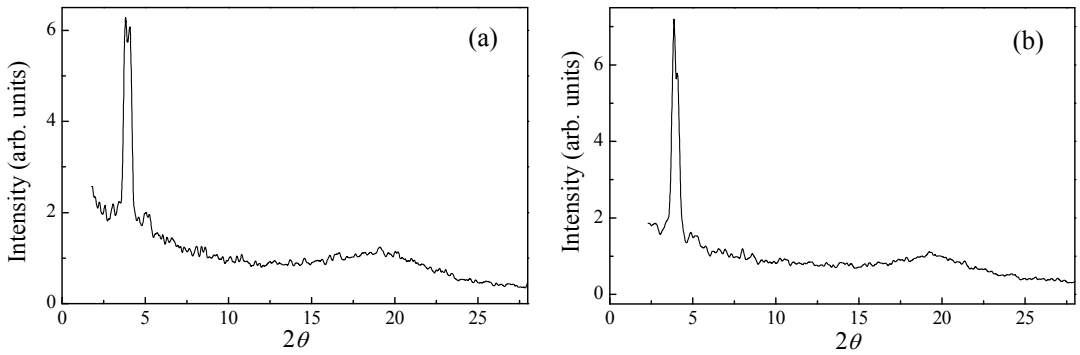

Figure S1. 1D intensity *vs* 2θ profiles obtained for the Col_r phase (a) at 70 °C (b) at 25 °C of **HBA-7.**

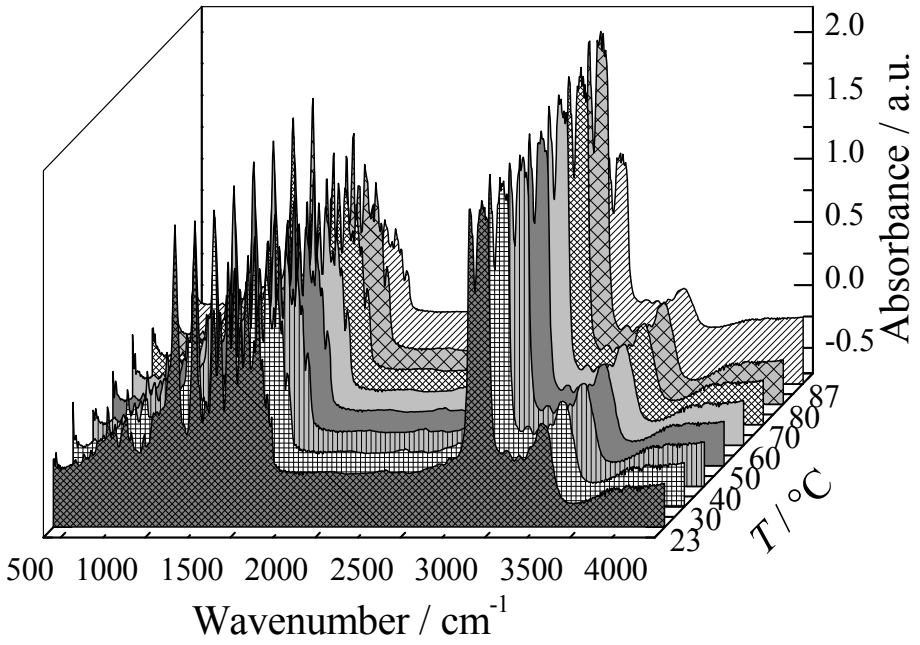

Figure S2. FTIR spectra obtained for the compound **HBA-10** as a function of temperature.

Table S1. CD spectroscopic data obtained for the hexacatenar bisamides **HBA-4** and **HBA-5**.

Compound	*T* /°C	CD	
		λ_{max} (nm)	Intensity (mdeg)
HBA-4	23	300.5	-26.9
	30	300.1	-26.5
	40	299.7	-24.5
	50	299.3	-24.9
	60	299.7	-23.3
	70	299.7	-27.1
	80	299.7	-25.6
	97	295.4	-6.88
HBA-5	24	304.1	+30.3
	30	304.2	+34.1
	40	304.5	+35.3
	50	305.3	+35.9
	60	304.9	+34.3
	70	305.1	+33.4
	80	305.1	+34.7
	97	304.7	+15.4

References

1 *(a)* C. V. Yelamaggad, G. Shanker, R. V. Ramana Rao, D. S. Shankar Rao, S. K. Prasad and V. V. Suresh Babu, *Chem. Eur. J,* 2008, **14**, 10462-10471; *(b)* G. Shanker, D. S. Shankar Rao, S. Krishna Prasad and C. V. Yelamaggad, submitted.