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Columnar mesophases constructed by hierarchical self-assembly of rod-like diacetylene molecules

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Table S1. Assignment of XRD data for the *m*DA mesophases [a]

Compounds	Mesophase structure	Spacing		Miller [b] indice
		d_{obs}/Å	d_{calcd}/Å	
9DA	D_L at 173 °C	27.89	27.85	(001)
	a = 27.89 Å	13.80	13.93	(002)
		9.13	9.30	(003)
		6.77	6.97	(004)
		5.04		
10DA	D_L at 166 °C	29.84	29.84	(001)
	a = 29.84 Å	14.93	14.92	(002)
		5.01		
	Col_{ro} ($P2_1/a$)	30.46	30.46	(110)
	at 144 °C	24.02	24.02	(020)
	a = 39.39 Å	14.45	14.83	(130)
	b = 48.05 Å	6.58	6.48	(270)
	Z = 14.98 for	5.07	5.10	(740)
	ρ = 1.0 g/cm^3	4.87		
		4.08		h_A
		3.71		h_B
11DA	D_L at 166 °C	32.14	32.14	(001)
	a = 32.14 Å	15.99	16.07	(002)
	d = 4.96 Å	10.61	10.71	(003)
		4.96		
	Col_{rd} ($P2_1/a$)	32.99	32.99	(110)
	at 153 °C	24.49	24.49	(020)
	a = 44.62 Å	16.34	16.33	(220)
	b = 48.98 Å	15.01	15.33	(130)
		10.42	10.74	(240)
		6.80	6.77	(270)
		4.88		
	Col_{ro} ($P2_1/a$)	33.09	33.09	(110)
	at 146 °C	23.63	23.63	(020)
	a = 46.36 Å	16.43	16.55	(220)
	b = 47.26 Å	14.79	14.92	(130)
	Z = 16.71 for	10.30	10.53	(240)
	ρ = 1.0 g/cm^3	6.66	6.48	(270)

		4.86		
		4.11		h_A
		3.76		h_B
12DA	D_L at 167 °C	33.55	33.55	(001)
	a = 33.55 Å	16.70	16.77	(002)
		11.11	11.18	(003)
		4.93		
	Col_{rd} ($P2_1/a$)	34.46	34.46	(110)
	at 153 °C	23.92	23.92	(020)
	a = 49.67 Å	17.03	17.23	(220)
	b = 47.84 Å	15.19	15.18	(130)
		6.82	6.59	(270)
		6.44	6.10	(740)
		4.86		
	Col_{ro} ($P2_1/a$)	34.78	34.78	(110)
	at 138 °C	23.10	23.10	(020)
	a = 52.84 Å	17.06	17.39	(220)
	b = 46.20 Å	15.03	14.79	(130)
	Z = 17.80 for	10.65	10.58	(240)
	ρ = 1.0 g/cm^3	6.67	6.40	(270)
		6.36	6.32	(740)
		4.83		
		4.10		h_A
		3.78		h_B
13DA	D_L at 166 °C	35.01	35.01	(001)
	a = 35.01 Å	17.35	17.50	(002)
		11.58	11.67	(003)
		4.91		
	Col_{rd} ($P2_1/a$)	36.06	36.06	(110)
	at 152 °C	24.00	24.00	(020)
	a = 54.63 Å	17.83	18.03	(220)
	b = 47.99 Å	15.50	15.35	(130)
		11.07	10.99	(240)
		6.56	6.65	(270)
		4.86		

	Col_{ro} ($P2_1/a$)	36.31	36.31	(110)
	at 135 °C	23.36	23.36	(020)
	a = 57.68 Å	18.00	18.16	(220)
	b = 46.73 Å	15.52	15.04	(130)
	Z = 18.87 for	11.10	10.83	(240)
	ρ = 1.0 g/cm^3	6.51	6.50	(270)
		4.82		
		4.11		h_A
		3.81		h_B
14DA	D_L at 165 °C	35.82	35.82	(001)
	a = 35.82 Å	17.76	17.91	(002)
		11.91	11.94	(003)
		4.91		
	Col_{rd} ($P2_1/a$)	37.73	37.73	(110)
	at 139 °C	24.10	24.10	(020)
	a = 60.62 Å	18.86	18.86	(220)
	b = 48.20 Å	15.96	15.53	(130)
		11.56	11.20	(240)
		6.56	6.71	(270)
		4.82		
16DA	D_L at 162 °C	38.41	38.41	(001)
	a = 38.41 Å	18.88	19.21	(002)
		12.61	12.80	(003)
		4.93		
	Col_{rd} ($P2_1/a$)	40.50	40.50	(110)
	at 135 °C	26.18	26.18	(020)
	a = 63.85 Å	20.07	20.25	(220)
	b = 52.38 Å	17.46	16.84	(130)
		12.38	12.12	(240)
		4.78		

[a] Phase nomenclature: D_L = discotic lamella mesophase, Col_{rd}, Col_{ro} = disordered and ordered rectangular columnar mesophases. The h_A and h_B indicate the stacking of cores and alkyl chains, respectively.

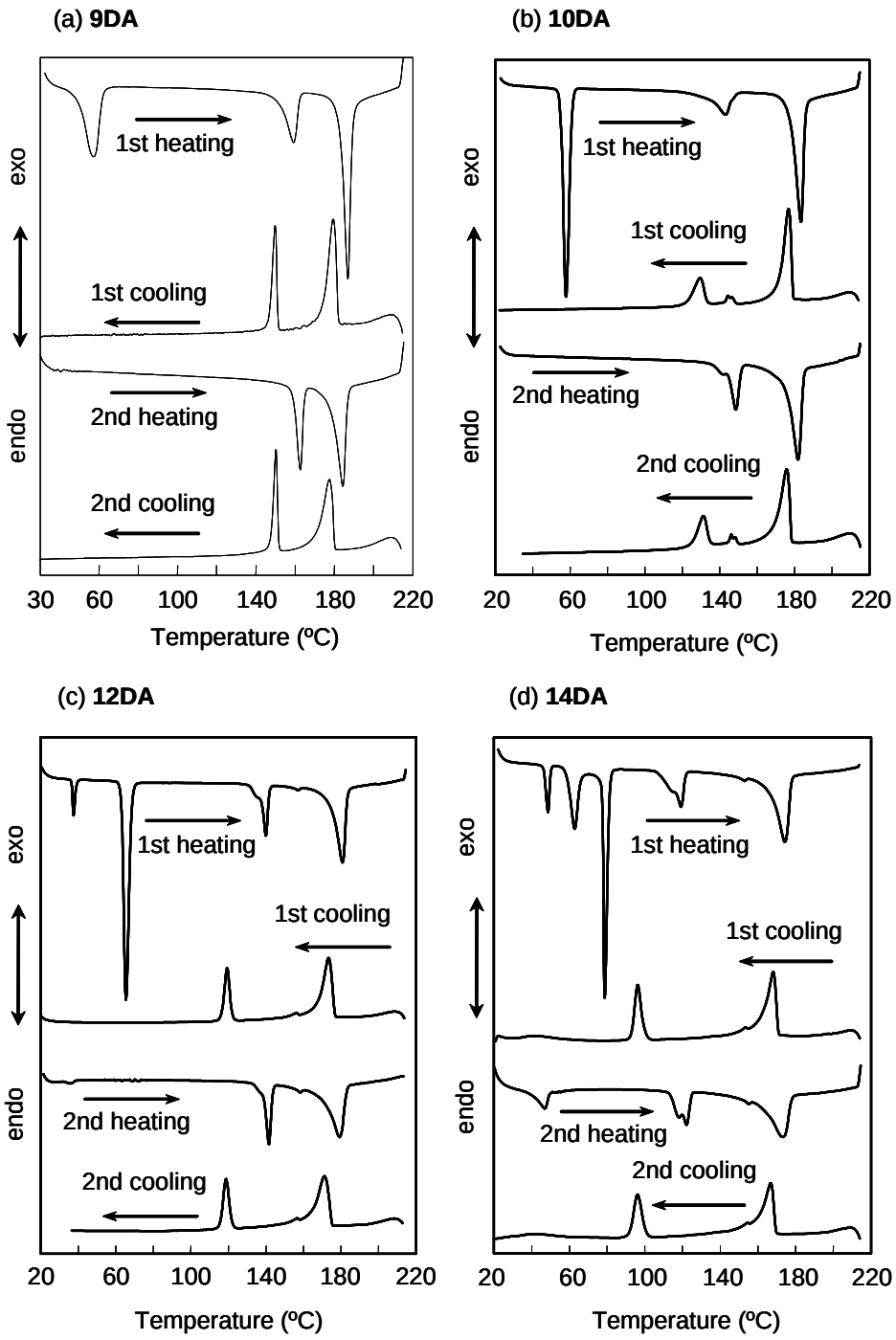

Figure S1. Repeated DSC traces of (a) **9DA**, (b) **10DA**, (c) **12DA**, and (d) **14DA**. The heating and cooling rates are 10 °C/min.

Experimental Section

Synthesis. All the ***m*DA**s were prepared by the Cadiot-Chodkiewicz coupling reaction of the corresponding 1-iodo-1-alkynes with 4-ethylbenzoic acid. The detailed procedures for the synthesis are described.

1-Iodo-1-tetradecyne. To a four-necked flask equipped with a dropping funnel, 1-tetradecyne (5 g, 0.026 mol) and 30 mL of a dry tetrahydrofuran (THF) were charged under an argon stream. The solution was cooled to 0 °C, and then 19.7 mL of nBuLi (1.57 mol/L in *n*-hexane) was added with a syringe. Iodine (7.8 g) in 30 mL of THF was added at room temperature and the mixture was further stirred for 2 h. The excess (nBuLi) was treated with 20 mL of water. The whole was extracted several timers with totally 1 L of *n*-hexane. The extracts were dried over Na_2SO_4. The product was purified by silica gel column chromatography with *n*-hexane. 1-Iodo-1-tetradecyne was obtained as slightly red liquid by the evaporation of the solvent. The yield was 90%.

1,3-Hexadecadiynyl-4-benzoic Acid (12DA). To a mixture of 9.6 mL of the 70% ethylamine aqueous solution, 5 mL of a distilled water, hydroxylamine hydrochloride (1.2 g), and copper(I) chloride (0.18 g), in a 200-mL four-necked flask under an argon stream, was dropwise added 4-ethylbenzoic acid sodium salt (2.88 g, 0.017 mol) in 30 mL of THF over 10 min, and then 1-iodo-1-tetradecyne (5.0 g, 0.016 mol) in 30 mL of THF over 30 min. After the solution was stirred overnight, the solvent was evaporated, and the HCl aqueous solution (1 mol/L) was added until the solution was acidic. The solution was extracted with 1 L of diethyl ether, and then the solvent was removed. The crude residue was purified by recrystallization from a mixture of THF and methanol. The **12DA** was obtained as a colorless powder in the yield of 89%. The other ***m*DA**s were similarly synthesized.

1,3-Dodecadiynyl-4-benzoic Acid (8DA): Yield 32%; colorless powder, T_{init} = 246.5 °C, Mp = 186.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.20 (s, CO_2H, 1H), 7.91 and 7.62 (d, J = 8.4 Hz, C_6H_4, 4H), 2.43 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.50,(q, C≡C$CH_2C\mathit{H}_2$, 2H) 1.35–1.25 (m, CH_2, 10H), 0.85 (t, J = 7.2 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.52 (CO_2H), 132.51, 131.15, 129.5, and 125.2 (C_6H_4), 87.48, 76.66, 73.78, and 64.53 (C≡C), 31.21, 28.54, 28.38, 28.24, 27.50, 22.05, and 18.69 (CH_2), 13.94 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$), 1693 ($\nu_{C=O}$,

dimer), 1424 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.51; H, 7.89%. Found: C, 80.81; H, 7.85%. 2θ(Cu Kα, crystals, r.t.) = 2.71, 4.72, 8.68, 9.45, 10.60, 11.64, 13.12, 13.53, 13.87, 17.19, 18.73, 21.90 and 22.96 deg.

1,3-Tridecadiynyl-4-benzoic Acid (9DA): Yield 45%; colorless powder, T_{init} = 270.2 °C, Mp = 157.7 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.20 (s, CO_2H, 1H), 7.93 and 7.65 (d, J = 8.1 Hz, C_6H_4, 4H), 2.44 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.54–1.26 (m, CH_2, 14H), 0.86 (t, J = 6.8 Hz, CH_3, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.57 (CO_2H), 132.55, 131.18, 129.54, and 125.24 (C_6H_4), 87.54, 76.70, 73.81, and 64.58 (C≡C), 31.29, 28.88, 28.67, 28.45, 28.26, 27.53, 22.13 and 18.73 (CH_2), 13.98 (CH_3); IR (KBr) 2411 ($\nu_{C\equiv C}$), 1688 ($\nu_{C=O}$, dimer) cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_2$: C, 80.94; H, 8.12%. Found: C, 81.04; H, 8.16%. 2θ(Cu Kα, crystals, r.t.) = 2.40, 4.81, 7.22, 16.13, 16.76, 20.29, 21.20, 22.13, 23.22 and 25.56 deg.

1,3-Tetradecadiynyl-4-benzoic Acid (10DA). Yield 36%; colorless powder. T_{init} = 273.7 °C Mp = 145.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, CO_2H, 1H), 7.92 and 7.63 (d, J = 8.4 Hz, C_6H_4, 4H), 2.43 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.55–1.26 (m, CH_2, 16H), 0.85 (t, J = 6.8 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.52 (CO_2H), 132.50, 131.14, 129.48, and 125.20 (C_6H_4), 87.48, 76.66, 73.77, and 64.54 (C≡C), 31.28, 28.92, 28.87, 28.66, 28.39, 28.21, 27.47, 22.09, and 18.68 (CH_2), 13.94 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$), 1701 ($\nu_{C=O}$), 1681 ($\nu_{C=O}$, dimer), 1427 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_2$: C, 80.92; H, 8.40%. Found: C, 81.25; H, 8.44%. 2θ(Cu Kα) = 2.40, 4.88, 7.33, 9.82, 16.08, 17.92, 19.15, 19.30, 19.87, 20.00, 20.94, 22.21, 23.79, 24.70 and 25.46 deg.

1,3-Pentadecadiynyl-4-benzoic Acid (11DA). Yield 30%; colorless powder. T_{init} = 261.7 °C, Mp = 148.6 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.21 (s, CO_2H, 1H), 7.93 and 7.64 (d, J = 8.4 Hz, C_6H_4, 4H), 2.44 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.56–1.25 (m, CH_2, 18H), 0.84 (t, J = 6.6 Hz, CH_3, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.56 (CO_2H), 132.55, 131.17, 129.53, and 125.24 (C_6H_4), 87.51, 76.70, 73.81 and 64.58 (C≡C), 31.33, 29.01, 29.01, 28.91, 28.75, 28.43, 28.25, 27.51, 22.13 and 18.72 (CH_2), 13.98 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$), 1701 ($\nu_{C=O}$), 1682 ($\nu_{C=O}$, dimer), 1429 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.58; H, 8.86%. Found: C, 81.44; H, 8.70%. 2θ(Cu Kα, crystals,

r.t.) = 2.28, 4.67, 6.95, 13.79, 16.05, 19.16, 19.79, 20.75, 22.07 and 23.61 deg.

1,3-Hexadecadiynyl-4-benzoic Acid (12DA): Yield 89%; colorless powder, T_{init} = 251.8 °C, Mp = 139.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.08 (s, CO_2H, 1H), 7.93 and 7.63 (d, J = 8.4 Hz, C_6H_4, 4H), 2.43 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.55–1.24 (m, CH_2, 20H), 0.85 (t, J = 6.8 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.63 (C=O), 132.61, 131.37, 129.39, and 125.40 (C_6H_4), 87.59, 76.84, 73.97, and 64.73 (C≡C), 31.41, 29.12, 29.06, 28.96, 28.81, 28.50, 28.34, 27.64, 22.19, and 18.87 (CH_2), 14.02 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$) 1701 ($\nu_{C=O}$), 1683 ($\nu_{C=O}$, dimer), 1411 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.48; H, 9.01%. Found: C, 81.61; H, 8.93%. 2θ(Cu Kα, crystals, r.t.) = 2.19, 4.50, 6.65, 13.33, 16.19, 18.26, 19.12, 19.77, 20.52, 21.41, 22.24, 23.88 and 25.46 deg.

1,3-Heptadecadiynyl-4-benzoic Acid (13DA): Yield 41%; colorless powder, T_{init} = 251.8 °C, Mp = 135.3 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.20 (s, CO_2H, 1H), 7.93 and 7.64 (d, J = 8.4 Hz, C_6H_4, 4H), 2.44 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.53–1.23 (m, CH_2, 22H), 0.84 (t, J = 6.8 Hz, CH_3, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.62 (C=O), 132.60, 131.23, 129.58, and 125.30 (C_6H_4), 87.57, 76.76, 73.86, and 64.64 (C≡C), 31.38, 29.16, 29.10, 29.04, 28.94, 28.81, 28.46, 28.28, 27.55, 22.18 and 18.78 (CH_2), 14.03 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$) 1700 ($\nu_{C=O}$), 1682 ($\nu_{C=O}$, dimer), 1429 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.94; H, 9.34%. Found: C, 81.61; H, 9.15%. 2θ(Cu Kα, crystals, r.t.) = 2.09, 4.19, 6.35, 12.67, 16.18, 17.16, 18.25, 19.09, 19.71, 20.33, 22.07, 23.50, 24.67 and 25.47 deg.

1,3-Octadecadiynyl-4-benzoic Acid (14DA): Yield 35%; colorless powder, T_{init} = 251.8 °C, Mp = 123.2 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.23 (s, CO_2H, 1H), 7.93 and 7.64 (d, J = 8.4 Hz, C_6H_4, 4H), 2.44 (t, J = 6.9 Hz, C≡CCH_2, 2H), 1.54–1.23 (m, CH_2, 24H), 0.85 (t, J = 6.6 Hz, CH_3, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.56 (C=O), 132.54, 131.17, 129.51 and 125.23 (C_6H_4), 87.52, 76.69, 73.80, and 64.59 (C≡C), 31.32, 29.07, 29.04, 29.02, 29.01, 28.96, 28.86, 28.73, 28.38, 28.21, 27.48, 22.12, and 18.71 (CH_2), 13.97 (CH_3); IR (KBr) 2242 ($\nu_{C\equiv C}$) 1702 ($\nu_{C=O}$), 1683 ($\nu_{C=O}$, dimer), 1428 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{25}H_{34}O_2$: C, 82.03; H, 9.56%. Found: C, 81.92; H, 9.35%.

2θ(Cu Kα, crystals, r.t.) = 2.01, 4.00, 6.07, 16.18, 19.01, 19.74, 20.81, 22.29, 23.69 and 25.27 deg.

1,3-Icosadiynyl-4-benzoic Acid (16DA): Yield 51%; colorless powder, T_{init} = 283.3 °C, Mp = 117.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, CO_2H, 1H), 7.92 and 7.62 (d, J = 8.4 Hz, C_6H_4, 4H), 2.43 (t, J = 6.8 Hz, C≡CCH_2, 2H), 1.55–1.23 (m, CH_2, 28H), 1.49 (t, J = 6.8 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.39 (C=O), 132.37, 131.20, 129.39, and 125.22 (C_6H_4), 87.37, 76.65, 73.79, and 64.52 (C≡C), 31.18, 28.91, 28.88, 28.86, 28.81, 28.71, 28.56, 28.25, 28.11, 27.43, 21.95, and 18.67 (CH_2), 13.78 (CH_3); IR (KBr) 2241 ($\nu_{C\equiv C}$) 1701 ($\nu_{C=O}$), 1682 ($\nu_{C=O}$, dimer), 1427 (coupling of O–H in-plane deformation and C–O stretching) cm^{-1}. Anal. Calcd for $C_{27}H_{38}O_2$: C, 81.91; H, 9.73%. Found: C, 82.18; H, 9.71%. 2θ(Cu Kα, crystals, r.t.) = 1.86, 3.74, 5.66, 9.51, 11.35, 16.13, 19.81, 20.51, 21.26, 22.38, 23.65 and 25.29 deg.

Measurements. The NMR spectra were recorded using a JEOL JMN A400 or Bruker AV300 spectrometer in dimethyl sulfoxide-d_6 (DMSO-d_6). The FT-IR spectra were recorded using a JASCO FT/IR 430 spectrometer equipped with a JASCO Intron IRT-30 infrared microscope and a Mettler-Toledo FP90 temperature controller. The fluorescence spectra were recorded using a JASCO FP-6600 spectrometer equipped with an HPC-503 temperature controller. The XRD data were collected using a Bruker MAC SAXS system with a Bruker Mo6X X-ray generator, a SAX optical system, a Hister detector, and a Mettler-Toledo FP900 temperature controller. The DSC was carried out using a Shimadzu DSC-50 or Seiko DSC 6200 calorimeter at the heating rate of 2, 5, and 10 °C/min. The phase transition behavior was observed by POM using a Nikon ECLIPSE E600 POL optical microscope equipped with a Hamamatsu PMA-11 detector and a Mettler-Toledo FP90 temperature controller.