

Supporting Information

Symmetric and Asymmetric Bolaamphiphiles from Ascorbic Acid

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Characterization of the synthesized products.

6-O-[(+)-L-ascorbic acid]-6'-O-[(+)-L-ascorbic acid] dodecanedioate

$R_f = 0.38$ [EtOAc/MeOH/H₂O (8:2:0.3)] (TLC detection by UV light and molybdate reagent). ¹H NMR (500 MHz, DMSO-*d*₆) δ : 1.22-1.30 (12H, m, CH₂) 1.52-1.58 (4H, m, CH₂) 2.30 (4H, t, $J = 7.4, 7.4$ Hz, CH₂) 3.94-3.97 (2H, ddd, $J = 1.8, 6.0, 11.5$ Hz, CH) 4.03-4.10 (4H, m, CH₂) 4.66 (2H, d, $J = 1.8$ Hz, CH). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 25.06 (CH₂) 29.13 (CH₂) 29.37 (CH₂) 29.52 (CH₂) 34.07 (CH₂) 65.13 (CH₂) 66.19 (CH) 75.70 (CH) 118.86 (C-O) 152.89 (C-O) 171.03 (C-O) 173.44 (C-O). FAB⁺-MS (m/z): 547 [M+H]⁺ 569 [M+Na]⁺. Elemental analysis: calc. C = 52.73%, H = 6.27%, found C = 52.72%, H = 6.37%.

6-O-[-D-isoascorbic acid]-6'-O-[-D-isoascorbic acid] dodecanedioate

$R_f = 0.38$ [EtOAc/MeOH/H₂O (8:2:0.3)] (TLC detection by UV light and molybdate reagent). ¹H NMR (500 MHz, DMSO-*d*₆) δ : 1.24 (12H, bs, CH₂) 1.48-1.54 (4H, m, CH₂) 2.28 (4H, t, $J = 7.4, 7.4$ Hz, CH₂) 3.96-4.02 (4H, m, CH₂) 4.03-4.06 (2H, m, CH) 4.73 (2H, d, $J = 2.3$ Hz, CH). ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 24.32 (CH₂) 28.43 (CH₂) 28.66 (CH₂) 28.81 (CH₂) 33.34 (CH₂) 63.35 (CH₂) 67.65 (CH) 76.19 (CH) 118.28 (C-O) 152.49 (C-O) 170.09 (C-O) 172.77 (C-O). FAB⁺-MS (m/z): 547 [M+H]⁺. Elemental analysis: calc. C = 52.73%, H = 6.27%, O = 41.00% found C = 53.10%, H = 6.80%.

6-O-[(+)-L-ascorbic acid]-vinyl dodecanedioate

¹H NMR (500 MHz, CD₃OD) δ : 1.22-1.30 (12H, m, CH₂) 1.64 (4H, m, CH₂) 2.60 (4H, m, CH₂) 3.99-4.11 (1H, ddd, $J = 2.0, 5.5, 7.0$ Hz, CH) 4.20 (4H, dd, $J = 5.5, 11.0$ Hz, CH₂) 4.27 (1H, dd, $J = 7.0, 11.0$ Hz, CH₂) 4.58 (1H, dd, $J = 1.5, 6.5$ Hz, CH₂vin) 4.65 (1H, d, $J = 2.0$ Hz, CH) 4.87 (1H, dd, $J = 1.5, 14.0$ Hz, CH₂vin) 7.28 (1H, dd, $J = 6.5, 14.0$ Hz, CHvin). ¹³C NMR (125MHz, DMSO-*d*₆) δ : 24.38, 24.74, 28.68, 28.79,

29.02, 29.14, 33.34, 33.59, 33.69, 34.10, 64.83, 66.00, 75.41, 98.10, 118.26, 141.49, 153.13, 170.73, 173.12, 175.11. FAB⁺-MS (*m/z*): 415 [M+H]⁺ 437 [M+Na]⁺. Elemental analysis: calc. C = 57.94%, H = 7.30%, O = 34.76% found C = 57.31%, H = 7.68%.

6-*O*-[(+)-L-ascorbic acid]-6'-*O*-[(-)-D-isoascorbic acid] dodecanedioate

$R_f = 0.38$ [EtOAc/MeOH/H₂O (8:2:0.3)] (TLC detection by UV light and molybdate reagent). ¹H NMR (400MHz, DMSO-*d*₆) δ : 1.20-1.30 (12H, m, CH₂) 1.45-1.55 (4H, m, CH₂) 2.20-2.35 (4H, m, CH₂) 3.90-4.10 (6H, m) 4.66 (1H, d, $J = 1.8$ Hz, CH) 4.75 (1H, d, $J = 2.1$ Hz, CH). ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 24.42 (CH₂), 24.46 (CH₂) 28.53 (CH₂) 28.79 (CH₂) 28.94 (CH₂) 33.40 (CH₂) 33.44 (CH₂) 63.44 (CH₂) 64.53 (CH₂) 65.54 (CH) 67.65 (CH) 75.07 (CH) 76.23 (CH) 118.23 (C-O) 118.33 (C-O) 152.26 (C-O) 152.59 (C-O) 170.23 (C-O) 170.43 (C-O) 172.83 (C-O) 172.86 (C-O). FAB⁺-MS (*m/z*): 547 [M+H]⁺ 569 [M+Na]⁺. Elemental analysis: calc. C = 52.73%, H = 6.27%, O = 41.00% found C = 53.10%, H = 6.80%.

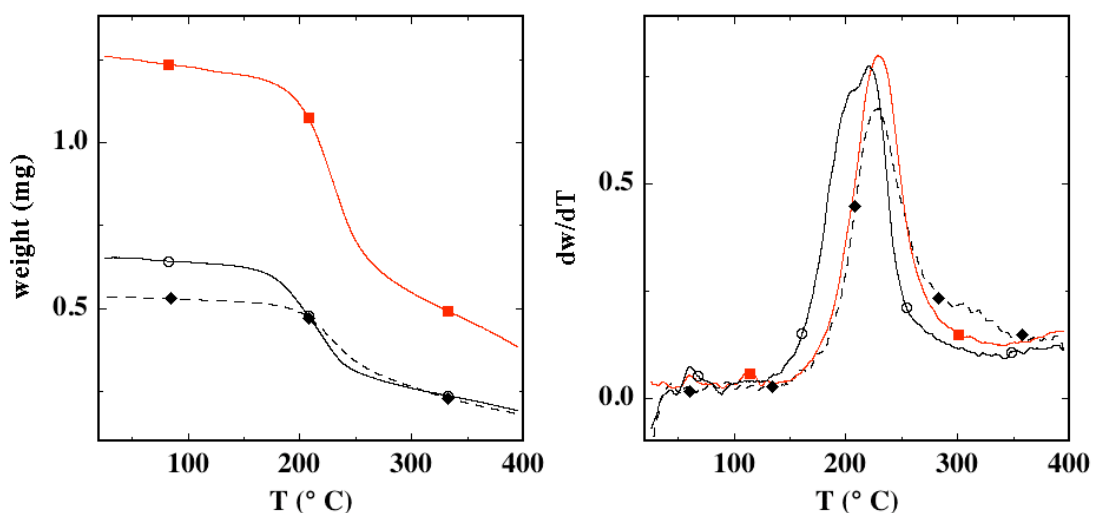


Figure S1. TGA profiles for freeze-dried pure solid bolaamphiphiles. DD: ○ (black full line); DL: ■ (red full line); LL: ◆ (black dotted line). Heating rate: 10° C/min.

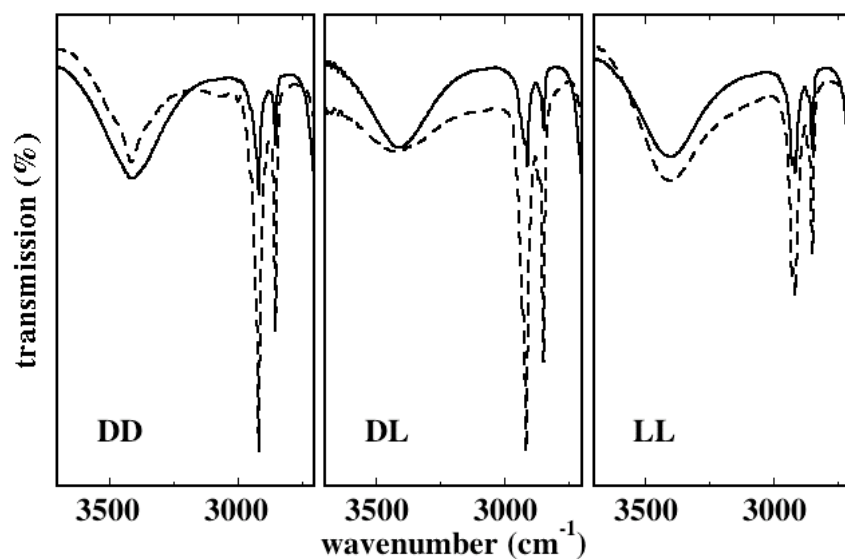


Figure S2. FTIR spectra between 3700 and 2700 cm^{-1} of DD, DL and LL dispersions (40% w/w) in D_2O in the liquid (full line) and coagel (dotted line) state.

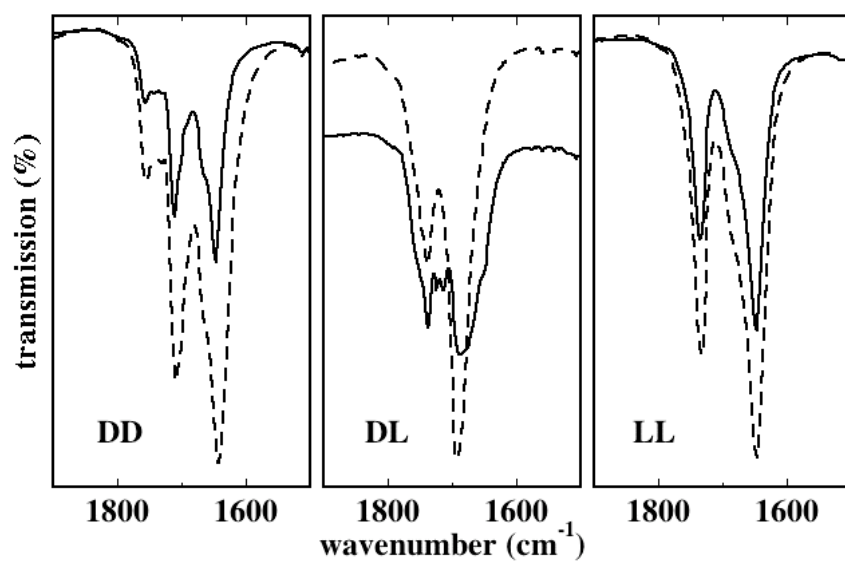


Figure S3. FTIR spectra between 1900 and 1500 cm^{-1} of DD, DL and LL dispersions (40% w/w) in D_2O in the liquid (full line) and coagel (dotted line) state.

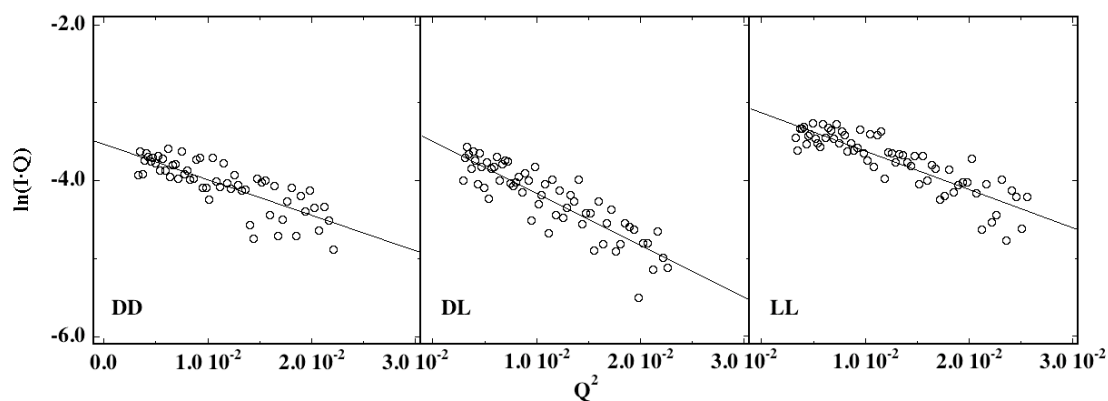


Figure S4. Modified Guinier plot for cylinders of DD, DL and LL dispersions (5% w/w) obtained for the liquid state.

Table S1. Length in the fully stretched conformation, spacings (in Å), 2θ values in brackets, and proposed chain packing according to Ref. 34, obtained from XRD experiments on the solid bolaamphiphiles.

	<i>DD</i>	<i>DL</i>	<i>LL</i>
<i>Full length</i> (Å)	20.16	24.52	25.37
<i>Long spacing</i> (Å)	20.16 (4.38°)	24.52 (3.60°)	25.37 (3.48°)
	3.35 (19.95°)		4.96 (17.88°)
<i>Short spacing</i> (Å)	4.02 (22.12°)		4.61 (19.28°)
	3.74 (23.72°)		4.07 (19.28°)
<i>Chain packing</i>	T		O⊥ or M

Table S2. Melting enthalpy (ΔH_{exp} , in J/g_{water}), fraction of bulk water (W_{bulk} , in % w/w), mean onset temperature of melting for bound freezing water (T_{onset} , in °C), fraction of bound freezing water (W_{bf} , in % w/w), percentage of strongly bound water (W_b , in % w/w), and number of strongly bound water molecules per headgroup (N_b).

	P	ΔH_{exp}	W_{bulk}	T_{onset}	W_{bf}	W_b	N_b
<i>DD</i>	2	323.9±0.4	94.3±4.0	-2.1±1.0	5.6±2.0	3.0±0.1	22.1±0.9
	5	320.7±2.1	88.9±4.7	-4.1±0.8	11.1±4.8	3.9±0.6	11.3±1.8
	10	308.9±2.2	78.0±8.7	-4.8±1.4	22.2±8.6	7.5±3.6	10.2±0.8
	20	295.9±5.6	50.4±6.1	-6.9±1.0	49.5±6.1	11.3±1.7	6.9±1.0
	30	298.3±2.2	51.3±0.0	-7.7±1.1	48.6±0.1	10.6±0.7	3.9±0.2
	40	263.1±1.3	5.9±3.1	-14.5±2.2	94.1±3.1	21.2±0.4	4.9±0.1
<i>DL</i>	2	325.2±0.8	95.2±0.3	-2.2±0.2	4.6±0.3	2.6±0.2	19.1±1.8
	5	320.8±2.1	88.3±3.8	-2.8±0.4	11.7±3.9	3.9±0.6	11.2±1.8
	10	312.7±4.7	79.7±7.2	-4.4±0.6	20.2±7.2	6.3±1.4	8.6±1.9
	15	305.4±7.7	70.0±0.3	-6.2±0.4	30.0±0.3	8.5±2.3	7.3±2.0
	20	298.6±12.1	61.7±13.1	-5.5±0.4	38.3±13.1	10.5±3.6	6.4±2.2
	30	291.6±0.5	44.5±2.3	-9.7±0.4	55.5±2.4	12.6±0.1	4.6±0.1
<i>LL</i>	40	261.0±13.9	7.0±2.9	-10.0±1.5	93.0±3.0	21.8±4.2	5.0±1.0
	2	324.3±0.2	96.0±0.6	-1.5±0.3	4.0±0.6	2.9±0.0	17.8±4.2
	5	321.7±1.9	93.9±1.9	-2.0±0.5	6.1±1.9	3.6±0.6	10.7±1.8
	10	316.5±3.9	90.0±3.1	-3.2±0.3	10.0±3.1	5.2±1.2	7.1±1.6
	15	307.9±0.1	87.7±0.1	-3.3±0.1	12.2±0.2	7.7±0.0	6.5±0.1
	20	298.0±0.9	70.5±4.5	-4.8±0.3	29.5±4.5	10.7±0.3	6.5±0.2
	30	287.7±0.1	76.3±0.2	-7.0±3.2	23.8±0.2	13.8±0.0	5.2±0.1
	40	255.4±4.5	17.3±8.5	-12.0±2.0	82.6±8.4	23.5±1.4	5.5±0.3

Table S3. Transition temperatures (T , in °C) and transition enthalpy changes (ΔH , in kJ/mol_{bola}) for DD, DL, and LL coagels in water as a function of the bolaamphiphile's concentration (P , in % w/w).

	<i>DD</i>		<i>DL</i>		<i>LL</i>	
P	T	ΔH	T	ΔH	T	ΔH
2	55.4±3.6	37.6±4.1	49.1±5.0	22.6±3.8	39.2±0.5	27.3±5.3
5	57.3±2.7	41.6±1.1	47.1±5.2	20.6±1.1	36.7±1.4	35.7±5.6
10	59.1±1.5	43.0±7.6	49.5±2.5	24.8±4.5	37.2±1.5	36.3±1.7
15	60.1±5.0	33.4±3.6	50.6±5.0	17.6±2.1	41.6±0.2	32.7±4.1
20	57.7±2.8	38.4±2.8	50.1±1.2	23.6±0.9	38.2±0.4	39.5±4.9
30	59.4±0.4	33.1±4.0	46.1±5.0	25.4±2.8	42.0±0.2	34.6±3.2
40	59.2±0.7	33.9±1.9	47.0±0.4	23.7±2.8	39.2±1.3	38.9±2.4