Control of Macroscopic Helicity Using the Sergeants and Soldiers Principle in Organogels

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Techniques:

$^1$H NMR spectra were measured on a Bruker Advance 300 spectrometer. The XWINNMR program was used for the pulse program. Circular Dichroism spectra were measured on a Jasco J-715. SEMs (Scanning Electron Microscopes) were recorded using a JEOL JSM 5410LV. Dried gel samples were
applied to polymer or stainless steel stubs by carbon tape. Prior to examination, the gels were coated with a thin gold layer by gold deposition (5 mA, 7 min).

**Materials:**
All chemicals and solvents were purchased from Aldrich or Tokyo Kasei Chemicals, and were used as received.

**Synthesis of compound 1:**

To a solution of \( p \)-phenylenediamine (98%, Aldrich) (2 g, 18.49 mmol) in 150 mL of dry \( \text{CH}_2\text{Cl}_2 \) were added slowly dodecanoyl chloride (>98%, TCI) (8.9 g, 40.49 mmol) and \( \text{Et}_3\text{N} \) (5.6 g, 55.48 mmol) by syringe and stirred for 3 h at 0°C to r.t. All the volatile components were evaporated. The crude product was purified by recrystallization to furnish 1 as a white solid (6.47 g, 74% yield).

\(^1\text{H NMR} \) (300 MHz, [D\(_6\)]DMSO, 80°C): 0.88 (6H, t, \( J = 6.8 \) Hz), 1.28 (24H, m), 1.61 (4H, m), 2.28 (4H, t, \( J = 7.41 \) Hz), 7.46 (4H, s), 9.42 (2H, s).


HRMS (EI+): calculated (C\(_{30}\)H\(_{52}\)N\(_2\)O\(_2\)) = 472.4029, found = 472.4030.

**Synthesis of compounds 2 and 3:**

Reagents and Conditions: (a) dodecanoyl chloride \( \text{Et}_3\text{N}, \text{CH}_2\text{Cl}_2 \), 3 h; (b) MeOH, KOH, CH\(_3\)OH, RT, 10 h; (c) phenylenediamine, EDC, DMAP, CH\(_2\)Cl\(_2\), 10 h.

**Synthesis of A**
To a solution of alanine methylester (98%, Aldrich) (1 g, 7.16 mmol) in 150 mL of dry \( \text{CH}_2\text{Cl}_2 \) were added slowly dodecanoyl chloride (>98%, TCI) (1.7 g, 7.88 mmol) and \( \text{Et}_3\text{N} \) (2.7 g, 21.49 mmol) by
syringe and stirred for 3 h at 0°C to rt. All the volatile components were evaporated and the residue was partitioned between CH$_2$Cl$_2$ and water. The organic phase was washed with water ($\times$3), and then dried in Na$_2$SO$_4$. The white solid was moved to 250 mL round-bottomed flask and KOH (1.2 g, 21.48 mmol) was added and stirred in 150 mL of CH$_3$OH for 10 h at rt. CH$_3$OH was evaporated and the residue was neutralized with 1 N HCl and filtered.

$^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$=0.85 (3H, t, $J$ = 6.87 Hz, CH$_3$), 1.24 (18H, m, CH$_2$), 1.46 (2H, s, br, CH$_2$), 2.07 (2H, t, $J$ = 7.47 Hz, COCH$_2$), 4.16 (1H, m, C*H), 8.07 (1H, d, $J$ = 7.32 Hz, NH), 12.45ppm (1H, s, br, COOH).

Synthesis of 2 and 3

To a solution of A (1.0 g, 3.89 mmol) in 50 mL of dry CH$_2$Cl$_2$ were added p-phenylenediamine (0.2 g, 1.85 mmol), EDC (744 mg, 3.89 mmol) and DMAP (474 mg, 3.89 mmol) and stirred 10 h. The white precipitates were obtained by filtration. The crude product was purified by washing with CH$_3$OH and CH$_2$Cl$_2$ to furnish 2 or 3 as a white solid (2.29 g, 52% yield).

$^1$H NMR (300 MHz, [D$_6$]DMSO, 80°C): $\delta$=0.85 (6H, t, $J$ = 6.99 Hz, CH$_3$), 1.23 (30H, m, CH$_2$), 1.49 (4H, m, CH$_2$), 2.12 (4H, t, $J$ = 7.41 Hz, COCH$_2$), 4.39 (2H, m, C*H), 7.51 (4H, s, ArH), 8.05 (2H, d, $J$ = 7.23 Hz, NH), 9.89 ppm(2H, s, NH).


HRMS (EI+): 2 calculated (C$_{36}$H$_{62}$N$_4$O$_4$) = 614.4771, found = 614.4761.

HRMS (EI+): 3 calculated (C$_{36}$H$_{62}$N$_4$O$_4$) = 614.4771, found = 614.4768.
Figure S1. SEM images of xerogels according to the different ratios of 2 and 1
All helices in SEM images show the $M$ helicity.

Figure S2. SEM images of xerogels according to the different ratios of 3 and 1
All helices in SEM images show the $P$ helicity.

Normalized CD data
Figure S3. Normalized CD and UV absorption spectra of 1 (black line), 2 (filled triangle), 3 (open triangle), 1:2 = 99:1 (filled square) and 1:3 = 99:1 (open square). UV spectra of 1:2 = 99:1 (black dashed line) and 2 (black solid line) in xerogel phase.