Supplementary Material (ESI) for Chemical Communications

Supplementary Information

New strategy for controlling the oligothiophene aggregation mode utilizing the gel-to-sol phase transition induced by crown-alkali metal interactions

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Measurements details

General: All chemical reagents were obtained from Aldrich, TCI, Kanto Chemicals or Wako were used without further purification. ^{1}H and ^{13}C NMR spectra were measured on JOEL ECS400 (400 MHz) spectrometers. Chemical shifts are recorded in ppm downfield from tetramethylsilane as the internal standard. FT-IR spectra were obtained using a Perkin–Elmer 100 instrument. Mass spectral data were obtained using a MALDI TOF Bruker autoflex II TOF/TOF mass spectrometer. Samples were prepared with dithrianol matrix. UV/Vis spectra were measured on a Shimadzu UV-2500PC spectrometer. Solution samples were measured in 1 cm length cell, gel samples were measured in 0.10 cm length cell. Fluorescence emission spectra were measured on a Perkin-Elmer LS55 instrument.

Gelation test of organic fluids: The gelator and the solvents were put in a capped test-tube sonicated about 3 min and heated until the solid was dissolved. The sample vial was cooled to 25 °C and left for 12 h at the ambient conditions. The state was evaluated by the "stable to inversion of a test tube" method.

Gelation test of organic fluids with alkali metal salts: The gelator, conc. solution of alkali metal salts in ethanol and the solvents were put in a capped test-tube sonicated about 3 min and heated until the solid was dissolved. The sample vial was cooled to 25 °C and left for 12 h at the ambient conditions. The state was evaluated by the "stable to inversion of a test tube" method.

Gel-sol transition temperature (T_{gel}): T_{gel} was measured by the test-tube-tilting method where a test tube containing the gel was immersed inversely in a thermostatted bath and the temperature was raised at 0.5°C/min. The T_{gel} was considered as the temperature when the mass was started to flow. The error involved in measuring T_{gel} was ±1 °C.

TEM and SEM measurements: The gel was put on a carbon-coated copper grid and dried in vacuo for 12 h at room temperature. Then, the xerogel sample was subjected to TEM observations with a FEI-TEM Philips TECNAI F20. For SEM observations, the xerogels were shielded by Pt and examined with a Keyence VE-9800 scanning electron microscope. The accelerating voltage of SEM was 20 kV.

AFM measurements: The gel was cast on a splintered mica plate with spin-coating (5000 rpm, 30 s). The sample was examined by S II NanoNavi/E-swap (non-contact mode).

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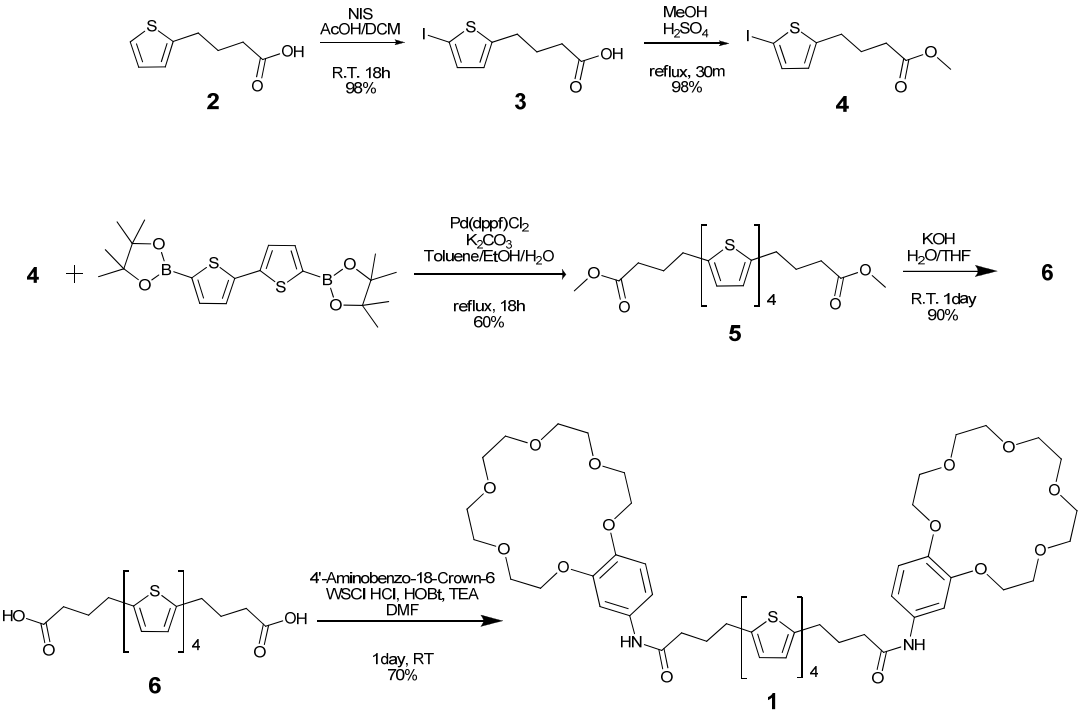
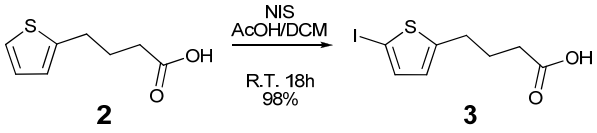
Synthesis details

General synthetic route.

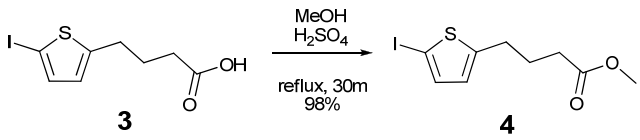


Reaction details



N-Iodosuccinimide (4.50g, 20.0mmol) was added under N_2 to a CH_2Cl_2 (dry) (50 mL) and glacial AcOH (50 mL) solution of 4-(thiophen-2-yl)butanoic acid 2 (3.40g, 20.0mmol), in a round-bottom flask, covered with aluminum foil. The mixture was stirred for 18h under N_2 at room temperature. The reaction was monitored by TLC Hex/AcOEt (7:3). After completion, the reaction mixture was poured to aqueous $Na_2S_2O_3$, organic phase was separated and evaporated under reduced pressure. Residue was dissolved in $CHCl_3$ (100ml), and was extracted by 1M NaOH (100mL x 2).The combined alkaline phases were acidified with 6M HCl to pH 2 and was extracted by $CHCl_3$ (100 mL × 3). The combined organic extract was dried over anhydrous $MgSO_4$, and evaporated to dryness to give a red oil of 3 (5.80g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.97 (q, 2H, CH_2), 2.41 (t, 2H, CH_2), 2.89 (t, 2H, CH_2), 6.50 (d, 1H, CH), 7.05 (d, 1H, CH), 10.1 (br. s, 1H, COOH).

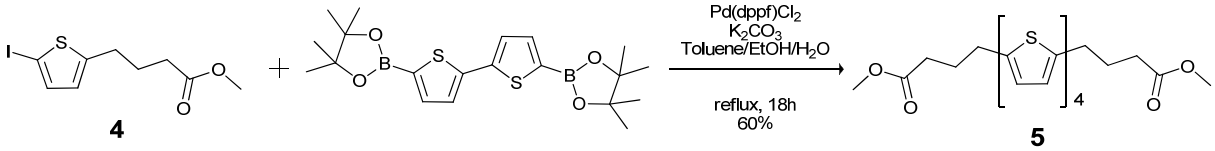


4-(5-Iodothiophen-2-yl)butanoic acid 3 (5.80g, 19.6mmol) was added to a MeOH (dry) (100 mL) and concentrated H_2SO_4 (150 µL) solution, in a round-bottom flask, under N_2. The mixture was stirred under reflux for 1h under N_2. The reaction was monitored by TLC Hex/AcOEt (7:3). After completion, the reaction mixture was evaporated under reduced pressure. After evaporation residue was dissolved in $CHCl_3$ (100ml) and was washed with saturated aqueous $NaHCO_3$ (100mL), dried over anhydrous $MgSO_4$, and evaporated to dryness to give a purple solid. The residue was chromatographed on silica with gradient Hex/AcOEt (95:5 – 9:1) as the eluent. Compound 4 was obtained as colourless oil (5.90g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.95 (q, 2H, CH_2), 2.34 (t, 2H, CH_2), 2.84 (t, 2H, CH_2), 3.65 (s, 3H, CH_3), 6.47 (d, 1H, CH), 7.02 (d, 1H, CH).

^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 26.6, (CH_2), 29.4 (CH_2), 33.0 (CH_2), 51.7 (CH_3), 70.1 (C-I), 126.5 (CH), 136.8 (CH), 150.5 (C-alkyl), 173.6 (C=O).

MALDI-TOF MS m/z 310.95, calc. for C9H12IO2S ($M+H^+$) found 311.10.

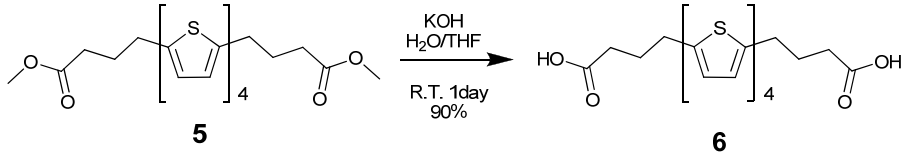


Mixture of a toluene (60ml), ethanol (15ml) and solution of K_2CO_3 (1.38g, 10mmol) in water (15ml) was bubbled with nitrogen stream during 1 hour. Methyl 4-(5-iodothiophen-2-yl)butanoate 4 (1.25g, 4mmol) followed by bithiophene bispinacol ester (0.83g, 2mmol) and Pd(dppf)Cl_2·DCM (0.15g, 0.2mmol) as a catalyst were added. Reaction was stirred under nitrogen atmosphere in reflux during 18 hours. Reaction progress were checked by TLC Hexane/Ethyl Acetate (4:1). Aqueous phase was separated by extraction. Organic layer dried over anhydrous $MgSO_4$, and evaporated to dryness to give a black solid. The residue was chromatographed on silica with Hex/AcOEt (9:1) as the eluent; a orange fraction of solid product 5 was isolated with 60% yield (0.6g).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.01 (q, 2H, CH_2), 2.39 (t, 2H, CH_2), 2.85 (t, 2H, CH_2), 3.68 (s, 3H, CH_3), 6.69 (d, 1H, CH), 6.98 (m, 2H, CH), 7.03 (d, 1H, CH).

^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, (CH_2), 29.5 (CH_2), 33.1 (CH_2), 51.7 (CH_3), 123.5 (CH), 123.8 (CH), 124.2 (C-H), 125.6 (C-H), 135.1, 135.6, 136.6, 143.8, 173.6 (C=O).

MALDI-TOF MS m/z 530.07, calc. for C26H26O4S4 (M+), found 530.12.



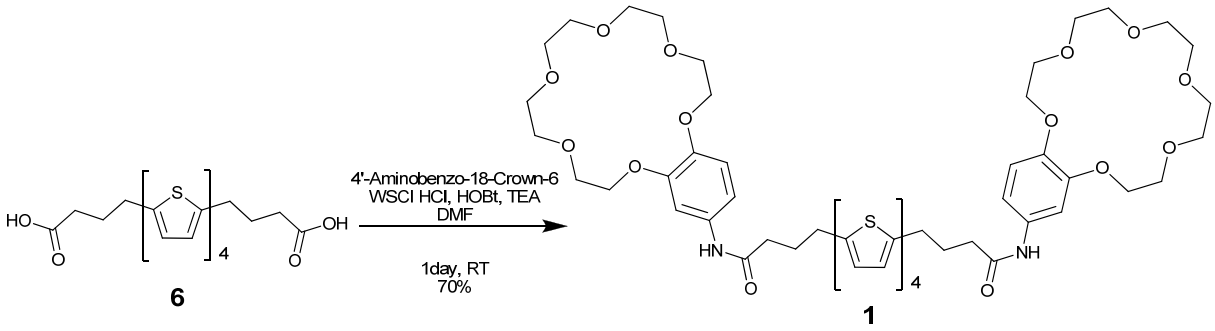
KOH (2.54g, 4.52mmol) dissolved in water (25ml) was added to a THF (200ml) solution of 5 (0.6g, 1.13mmol). Reaction was stirred in room temperature one day. Reaction progress was checked by TLC plate Hex/AcOEt (4:1).

After sedimentation of orange solid product, THF was removed. Orange solid of 5 potassium salt was dissolved in water (250ml). Aqueous solution was acidified to pH-2 with 6M HCl. After filtration and drying under vacuum dark orange solid of product 6 was obtained in 90% yield (0.51g).

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) 1.85 (q, 2H, CH_2), 2.29 (t, 2H, CH_2), 2.81 (t, 2H, CH_2), 6.83 (d, 1H, CH), 7.16 (d, 1H, CH), 7.19 (d, 1H, CH), 7.26 (d, 1H, CH), 12.13 (bs, 1H, COOH).

^{13}CNMR (100 MHz, d_6-$DMSO_3$): δ (ppm) 26.9, (CH_2), 29.2 (CH_2), 33.3 (CH_2), 124.6 (CH), 124.9 (CH), 125.5 (C-H), 126.5 (C-H), 134.1, 134.2, 136.3, 144.8, 174.6 (C=O).

MALDI-TOF MS m/z 502.04, calc. for C24H22O4S4 (M+) found 502.19.



WSCl HCl (0.5g, 3.06mmol) and HOBt (0.42g, 3.06mmol) were added to a DMF solution of 6 (0.51g, 1.02mmol) with 4'-aminobenzo18-crown-6 (1.0g, 3.06mmol) and TEA (1.3ml, 10.2mmol). Reaction was stirred under N_2 flow in room temperature during 1 day. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was dissolved in $CHCl_3$ (100ml) and treated with 1 M aqueous HCl (200ml), washed with aqueous $NaHCO_3$ (200ml) and brine (200ml), dried over anhydrous $MgSO_4$, and then evaporated to dryness. The residue was chromatographed on alumina with $CHCl_3$/MeOH (97:3) as the eluent; a orange fraction of 1 was isolated with 70% yield (0.8g).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.12 (q, 2H, CH_2), 2.37 (t, 2H, CH_2), 2.90 (t, 2H, CH_2), 3.64-3.78 (bm, 12H, -OCH_2 CH_2O-), 3.89 (m, 4H CH_2), 4.10-4.18 (bm, 4H, PhO-CH_2), 6.72 (d, 1H, CH), 6.77-6.87 (m, 2H, CH), 6.98 (t, 2H, CH), 7.03 (d, 1H, CH), 7.14 (bs, 1H, NH), 7.32 (d, 1H, CH).

^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 26.9, (CH_2), 29.4 (CH_2), 36.3 (CH_2), 68.9, 69.5, 69.6, 70.8, 70.9, 107.0, 112.2, 114.7, 123.5, 123.9, 124.2, 125.7, 132.1, 135.1, 135.6, 136.6, 143.9, 145.7, 149.3, 170.4 (C=O).

MALDI-TOF MS m/z 1120.35, calc. for C56H68N2O14S4 (M^+) found 1120.87; 1143.34, calc. for C56H68N2O14S4Na (M+Na^+) found 1143.88; 1159.32, calc. for C56H68N2O14S4K (M+K^+) found 1159.88.

IR of the dry gel (cm^{-1}): 3280 (ν_{N-H}), 3067 (ν_{C-H}), 1444, 1410 ($\nu_{C=C}$), 1370, 1258 (ν_{C-H}), 1013-1130 (ν_{C-C}), 845-863 (ν_{C-O-C}), 790 (ν_{C-H}, ν_{C-S-C}).

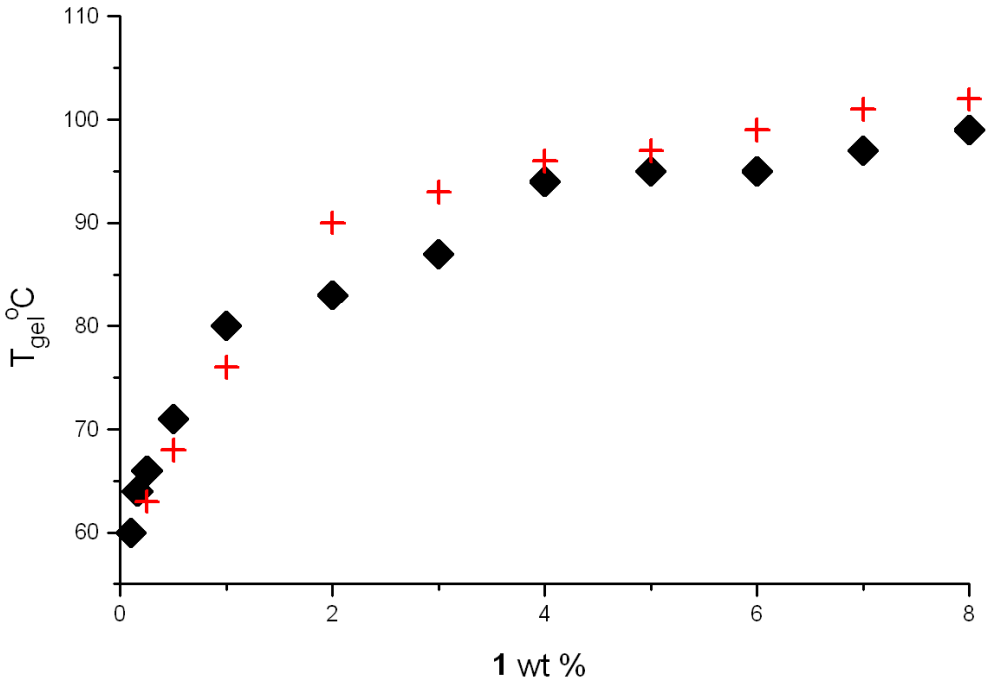


Fig. S1 T_{gel} changes with concentration of **1** from: EtOH/$CHCl_3$ (8:2) – (square) and *n*-PrOH/$CHCl_3$ (8:2) - (cross).

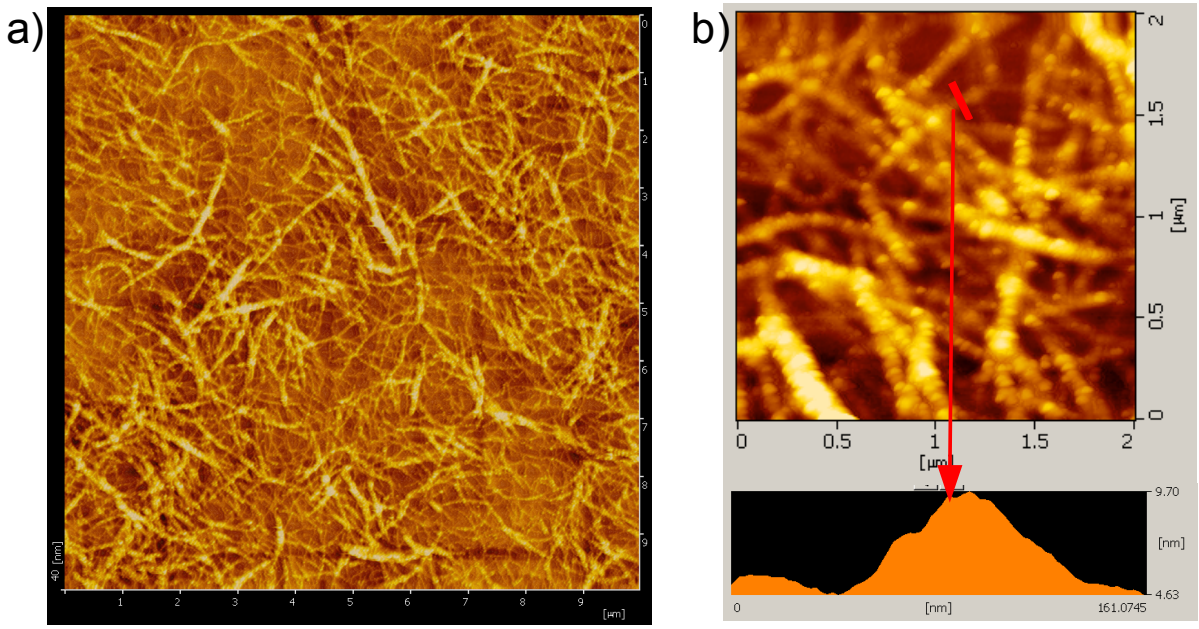


Fig. S2 (a) AFM image of nano-fibre structure of the gel of **1** 0.25 wt% - EtOH/$CHCl_3$ (8:2); (b) Nano-fibre height measurements.

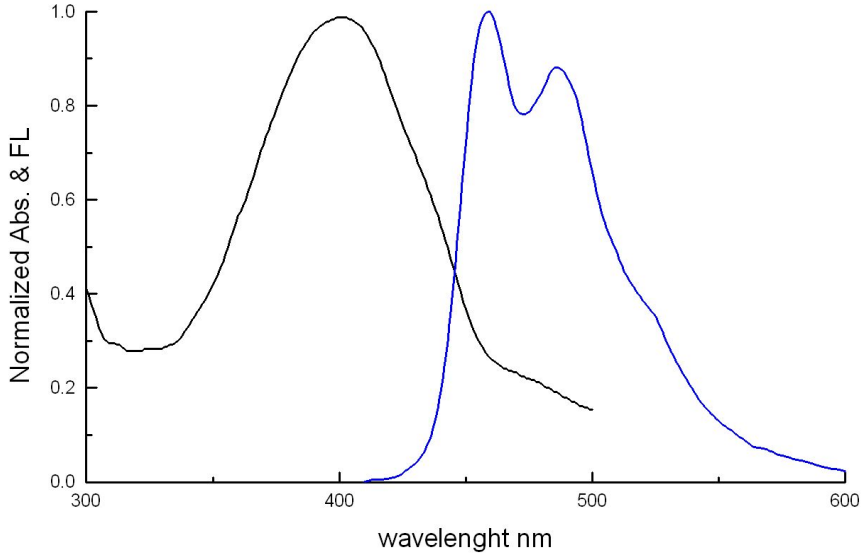


Fig S3 Normalized absorption (black) and fluorescence (blue) spectra in EtOH (8.6 μmol dm^{-3}).

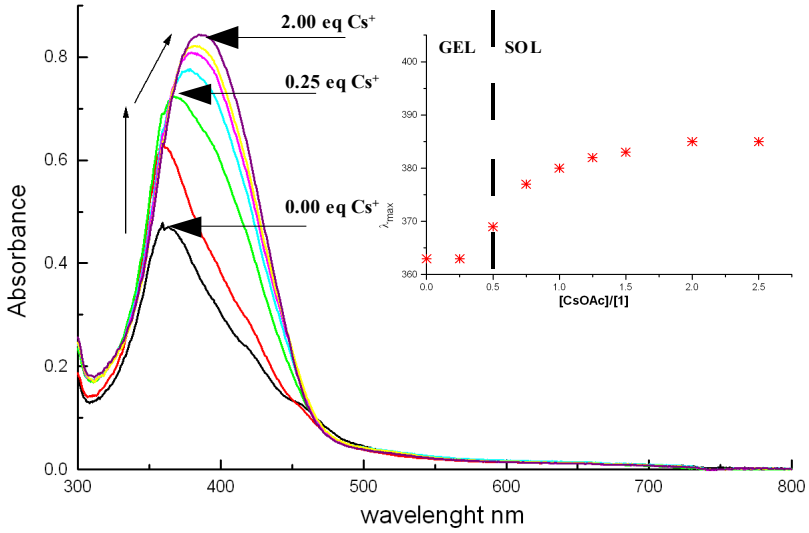


Fig. S4 UV/Vis titration of the gel of **1** 0.25%wt by CsOAc in EtOH/$CHCl_3$ (8:2). Inset: λ_{max} changes with increasing concentration of CsOAc and the gel-to-sol phase transition.