Supporting Information

Spectroscopic, Microscopic and first Rheological investigations in Charge-transfer interaction induced Organogels

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Figure S5. (a) Dynamic frequency sweep experiment (at a constant stress of 6 Pa) and (b) stress sweep experiment (at a frequency of 1 Hz) with 1-octanol gels of 4/TNF (1:1) (square) and 4/TNF (1:0.5) (circle).

References
Scheme S1. Synthetic routes for 1 and 2.

Scheme S2. Synthetic route for 3.

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Synthesis of esters S1-S5 and S7.

The synthesis of esters S1, S2, and S7 was achieved from the corresponding acids following the standard procedure of refluxing with MeOH/H₂SO₄. Compounds S1 and S2 are known in the literature.¹ For the column purification of S7, 3 % EtOAc/hexanes was used as the eluent, affording the pure ester S7 in 90 % yield (light yellow liquid).¹ ¹H NMR (300 MHz, CDCl3): δ (ppm) 2.19 (2H, m), 2.47 (2H, t), 3.39 (2H, t), 3.69 (3H, s), 7.79 (1H, d), 7.84-8.28 (7H, m), 8.33 (1H, d).

Starting from anthracene, ester S3 was synthesized following a reported procedure.²

Starting from phthalic anhydride, standard protocols³ were followed to obtain anthraquinone-2-carboxylic acid, which was converted to ester S4 following a literature procedure.⁴

Starting from 9-anthracencarbinol, ester S5 was obtained in 4 steps following a literature procedure.⁵

General procedure for the synthesis of the carboxamides 1-6.

The ester (0.2 mmol) was taken in a 10 mL rb flask, to which TRIS (0.3 mmol) and K₂CO₃ (0.3 mmol) were added. After adding DMSO (0.3 mL), the reaction mixture was stirred at 70 °C for 24 h. The solvent was removed in vacuo, and the residual solid was adsorbed on silica using MeOH (dry packing) and purified on a silica gel (100-200 mesh) column using 30-80 % EtOAc/CHCl₃ as the eluent.

Following this procedure, carboxamide 1 was obtained in 74 % yield (white amorphous solid). Mp 149-152 °C. IR (KBr, cm⁻¹): 3277 (br), 1630. ¹H NMR (300 MHz, DMSO-d₆): δ 3.53 (6H, d, J = 5.4 Hz), 3.97 (2H, s), 4.72 (3H, t, J = 5.4 Hz), 7.42-7.52 (5H, m), 7.78-7.92 (2H, m), 8.05 (1H, unresolved d).¹³C NMR (75 MHz, DMSO-d₆): δ 171.76, 133.43, 132.92, 132.14, 128.46, 127.85, 127.21, 126.09, 125.76, 125.61, 124.36, 62.48, 60.75. Anal. Calcd for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.08; H, 6.76; N, 4.99. LRMS: TOF EI-MS 312 (M⁺ + Na).

Carboxamide 2 was obtained in 53 % yield (white amorphous solid). Mp 126-128 °C.¹H NMR (300 MHz, DMSO-d₆): δ 1.38 (3H, d, J = 6.9 Hz), 3.52-3.55 (6H, m), 3.84 (3H, s), 3.86 (1H, q), 4.72 (3H, t, J = 5.4 Hz), 7.10-7.14 (1H, m), 7.22 (1H, s), 7.25 (1H, unresolved d), 7.42-7.45 (1H, m), 7.71 (1H, br s), 7.74 (1H, s), 7.77 (1H, s).¹³C NMR (75 MHz, DMSO-d₆): δ 175.06, 157.10, 137.44, 133.21, 129.23, 128.48, 126.73, 126.60, 125.43, 118.64,
105.78, 62.20, 60.74, 55.24, 45.27, 18.84. Anal. Calcd for C₁₈H₂₃NO₅·₁/₂H₂O: C, 63.14; H, 7.07; N, 4.09. Found: C, 63.16; H, 6.70; N, 4.36. LRMS: TOF EI-MS 356 (M⁺ + Na).

Carboxamide 3 was obtained in 63 % yield (deep yellow amorphous solid). Mp 178-179 °C. IR (KBr, cm⁻¹): 3340, 3303, 3052, 2931, 2873, 1627, 1610, 1523. ¹H NMR (300 MHz, DMSO-d₆): δ 3.80 (6H, d, J = 5.4 Hz), 4.84 (3H, t, J = 5.4 Hz), 7.49-7.63 (5H, m), 8.05-8.17 (3H, m), 8.62 (1H, s), 8.93 (1H, s). ¹³C NMR (100 MHz, DMSO-d₆): δ 170.09, 136.01, 131.86, 131.60, 131.54, 130.39, 128.91, 128.34, 128.19, 126.90, 126.46, 126.38, 125.35, 124.97, 124.87, 63.61, 60.88, 60.79. Anal. Calcd for C₁₉H₁₉NO₄: C, 70.14; H, 5.89; N, 4.30. Found: C, 70.17; H, 6.07; N, 4.51. LRMS: TOF EI-MS 348 (M⁺ + Na).

Carboxamide 4 was obtained in 67 % yield (deep yellow amorphous solid). Mp 200-202 °C. IR (KBr, cm⁻¹): 3380, 3329, 3254, 2945, 2884, 1639, 1519. ¹H NMR (300 MHz, DMSO-d₆): δ 3.78 (6H, d, J = 4.8 Hz), 4.88 (3H, br s), 7.56-7.59 (3H, m), 7.85 (1H, d, J = 8.7 Hz), 8.14 (3H, unresolved t), 8.62 (2H, d, J = 9.9 Hz), 8.73 (1H, s). ¹³C NMR (75 MHz, DMSO-d₆): δ 167.54, 132.24, 132.06, 131.67, 130.12, 128.25, 127.79, 126.47, 126.07, 123.85, 62.96, 60.52. MS: Calcd for C₁₉H₁₉NO₄ + Na: 348.1207. Found: 348.1212.

Carboxamide 5 was obtained in 55 % yield (pale yellow amorphous solid). Mp 210-212 °C. IR (KBr, cm⁻¹): 3373, 3340, 3051, 2885, 2840, 1633, 1525. ¹H NMR (300 MHz, DMSO-d₆): δ 4.58 (2H, s), 4.77 (3H, t, J = 5.4 Hz), 7.47-7.56 (4H, m), 7.63 (1H, s), 8.06-8.09 (2H, m), 8.29 (2H, unresolved d), 8.52 (1H, s). ¹³C NMR (100 MHz, DMSO-d₆): δ 171.57, 131.21, 130.58, 128.92, 128.88, 126.41, 125.97, 125.22, 125.09, 62.53, 60.80, 35.07. MS: Calcd for C₂₀H₂₁NO₄ + Na: 362.1368. Found: 362.1366.

Carboxamide 6 was obtained in 60 % yield (pale yellow amorphous solid). Mp 173-175 °C. IR (KBr, cm⁻¹): 3275, 3042, 2939, 2876, 1643, 1550. ¹H NMR (300 MHz, DMSO-d₆): δ 1.98 (2H, t), 2.29 (2H, t, J = 7.2 Hz), 3.30 (2H, t, J = 7.6 Hz), 4.83 (3H, t, J = 5.4 Hz), 7.17 (1H, s), 7.93 (1H, d, J = 3.9 Hz), 8.01-8.10 (3H, m), 8.18-8.27 (4H, m), 8.36 (1H, d, J = 4.5 Hz). ¹³C NMR (100 MHz, DMSO-d₆): δ 173.84, 136.79, 131.05, 130.59, 129.47, 128.31, 127.77, 127.64, 127.41, 126.69, 126.35, 125.14, 125.12, 124.98, 124.40, 124.31, 123.70, 62.44, 60.90, 35.80, 32.27, 27.90. MS: Calcd for C₂₄H₂₅NO₄ + Na: 414.1681. Found: 414.1676.

**Synthesis of 7-11**

Compounds 7-11 were prepared following reported procedures.⁶
Gelation test

A weighed amount of the gelator (with or without one equivalent of TNF) in an organic liquid was heated in a sealed tube to a homogenous solution. The solution was then cooled either in air or by dipping in ice-water bath. The gel formation was observed within a few minutes.

Gel-sol transition temperature ($T_{gel}$)

The gel-sol transition temperature ($T_{gel}$) was recorded by the inverted test tube method. Gels prepared in sealed tubes (diameter 8 mm, gel volume 0.3 or 0.4 mL) were kept upside down in thermostat and the temperature of the thermostat was raised slowly (2°C/min). The temperature at which the gel fell under gravity was noted as the $T_{gel}$.

For the comparison of thermal stability in different solvents, all the CT gels were made with 1:1 mol ratio of donor:TNF. The CT gels based on donors 3-5 were prepared in 0.4 mL of solvent. Before commencing the experiment, the 3/TNF gels were stabilized for 1 h, whereas the gels of 4/TNF and 5/TNF were stabilized for 6 h. The CT gels of 7-9 were made in 0.3 mL of solvent and stabilized for 12 h.
Variable temperature spectral study

Appropriate amounts of the anthracene derivative and TNF were dissolved in the gelling solvent by heating and transferred to a quartz cuvette of 1 mm path length for variable temperature UV studies, whereas for the variable temperature fluorescence studies, a quartz cuvette of 2 mm path length was used. For preparing the CT gels of 3-5, the cuvette was again heated to ~ 120 °C and then dipped in ice-water bath for ~ 2 min. After that, the cuvette was allowed to come to rt (~ 28 °C) and the already formed gel was stabilized for ~ 20 min. before the experiment. The gel was then heated in steps of 5 °C, and kept at each temperature for ~ 20 min, before recording the absorbance/fluorescence. For the CT gels of 7-9, the cuvette with the hot sol was kept at rt to allow gel formation. The gels were stabilized at rt for 6h. The temperature was varied from 25°C to 65°C and the spectra were recorded at 5°C intervals (at each temperature, the system was equilibrated for 10 min).

Rheology

Dynamic rheological measurements were done on the gels on a AR 1000 rheometer (TA instruments) using plate-plate (hatched) geometry (20 mm diameter, 400 μm gap). For measurements on the CT gels derived from the donors 3-5, the rheometer stage was pre-cooled to 5 °C (for 1-octanol gels) or 10 °C (for 1-decanol gels) and the hot sols (~ 120 °C) were quickly placed over the stage using a pre-heated pasteur pipette (~ 0.5 mL). The stage was kept at this temperature for further 2 min. and then heated up to 25 °C. The gel on the stage was stabilized for ~ 15 min. (for 4/TNF gels) or ~ 30 min. (for 3/TNF and 5/TNF gels) at 25 °C. The geometry gap was then set and the experiment was started immediately. For the CT gels of 7-9, the gel was introduced on the stage (at 25 °C) as a hot sol and immediately after gel formation, the geometry gap was set. The gel was then stabilized for 15 min. before starting the experiment.

Scanning Electron Microscopy

The gels were melted to make sols and these sols were drop cast (~ 10-100 μL) on the carbon tape of SEM holders. After initial drying in air for a few hours, they were kept under high vacuum for several hours. Then the xerogels were gold coated (10 nm thick) using a BAL-TEC SSD-500 sputter coater instrument and imaged.
Transmission Electron Microscopy

The gels were melted to sols and 10 μL of the sols were drop-cast onto a carbon coated copper grid and allowed to dry at rt for a few hours. Then an aqueous 0.1% uranyl acetate solution was drop-cast on the samples and allowed to dry at rt for a few more hours. Finally the samples were further dried under high vacuum for 5-6 h before imaging.

Confocal Fluorescence Microscopy

The confocal fluorescence microscopy (CFM) measurements were performed on a Picoquant Microtime 200. The Ti-Sa laser chain includes a Coherent Mira and a frequency doubler and affords pulses of 4-6 ps at 385 nm. The beam is injected by 90° reflection on a dichroic mirror in the microscope and the emission is detected by a time-resolved avalanche photodiode (MPD). The room is thermostated at 23°C with air-conditioning. The Picoquant Symphotime software is used to image the fluorescence intensity.

Figure S1. Variation of the emission spectra on heating a gel of 3/TNF (3:2) in 1-decanol (conc. of 3 : 17 mM). $\lambda_{ex} = 360$ nm.

Variable Temperature Fluorescence Spectra of 4/TNF gel in 1-pentanol.

Figure S2. Variation of the emission spectra on heating a gel of 4/TNF (1:1) in 1-pentanol (conc. 12.3 mM). $\lambda_{ex} = 360$ nm.
Variable Temperature Fluorescence Spectra of 5/TNF gel in 1-octanol.

**Figure S3.** Variation of the emission spectra on heating a gel of 5/TNF (1:1) in 1-octanol (conc. 11.8 mM). $\lambda_{ex} = 360$ nm.

Absorption Spectrum of TNF in CHCl₃.

**Figure S4.** Absorption spectrum of TNF in CHCl₃ (2.4 mM).
Comparison of the results of the rheology experiments for the 1-octanol gels of 4/TNF (1:1) and 4/TNF (1:0.5):

Figure S5. (a) Dynamic frequency sweep experiment (at a constant stress of 6 Pa) and (b) stress sweep experiment (at a frequency of 1 Hz) with 1-octanol gels of 4/TNF (1:1) (square) and 4/TNF (1:0.5) (circle).

References


