

Supporting Information

Charge-transfer Interaction Mediated Organogels from Bile acid Appended Anthracenes: Rheological and Microscopic studies

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Coupling of 2,3-Dihydroxyanthracene¹ and iodobile derivatives²

Preparation of **2** : 2,3 dihydroxy anthracene (0.24 mmol) was taken in 10 mL rb flask, to which DMF (3 mL) and K₂CO₃ (1.2 mmol) were added and stirred for 30 min at 60 °C. After the addition of the iodobile derivative (0.61 mmol) dissolved in THF (3 mL) to the reaction mixture, stirring was continued for 16 h. The solvent was removed under vacuum and the crude was adsorbed silica and column chromatographed to obtain the pure product. All the compounds (**2**, **3** and **4**) were prepared by this following this procedure.

Compound	Eluent	Yield (%)
2	20 % EtOAc/CHCl ₃	33
3	90 % EtOAc/CHCl ₃	24
4	10 % EtOH/ CHCl ₃	51

Compound 2:

Pale yellow solid

mp: 144-146 °C

¹H NMR (300 MHz, CDCl₃) δ: 8.19 (s, 2H), 7.91 (m, part of AA'BB', 2H), 7.38 (m, part of AA'BB', 2H), 7.18 (s, 2H), 4.16 (m, 4H), 3.64 (m, 2H), 2.17-1.21 (br. m, 54H, steroidal CH, CH₂), 1.07 (d, J = 6.3 Hz, 6H), 0.94 (s, 6H), 0.70 (s, 6H)

¹³C NMR (75 MHz, CDCl₃) δ: 150.02, 130.68, 128.72, 127.57, 124.34, 123.65, 105.70, 71.87, 66.90, 56.52, 56.44, 42.85, 42.09, 40.47, 40.17, 36.45, 35.86, 35.35, 35.05, 34.58, 33.42, 30.56, 28.28, 27.21, 26.45, 24.30, 23.37, 20.82, 19.24, 12.07.

IR (KBr): 3319, 2929, 2863, 1489, 1466, 1219, 1163.

[α]_D²⁵ +37 (1, CHCl₃)

HRMS: Calcd. for C₆₀H₈₆O₄Na: 893.6424; found: 893.6443

Compound 3:

Pale yellow solid

mp: 172-174 °C

¹H NMR (300 MHz, CDCl₃) δ: 8.18 (s, 2H), 7.91 (m, part of AA'BB', 2H), 7.38 (m, part of AA'BB', 2H), 7.17 (s, 2H), 4.15 (m, 4H), 4.03 (m, 2H), 3.6 (m, 2H), 2.11-1.23 (br. m, 52H, steroidal CH, CH₂), 1.12 (d, J = 6 Hz, 6H), 0.91 (s, 6H), 0.73 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ: 151.10, 130.74, 128.74, 127.60, 124.38, 123.71, 105.92, 73.06, 71.84, 66.88, 48.26, 47.68, 46.67, 42.15, 36.52, 36.08, 35.31, 34.74, 34.16, 33.76, 33.04, 30.63, 28.61, 27.27, 27.18, 26.19, 23.73, 23.17, 18.34, 12.86.

IR (KBr): 3403, 2936, 2864, 1466, 1163, 1042

[α]_D²⁵ -19.7 (1, CHCl₃)

HRMS: Calcd. for C₆₀H₈₆O₆Na: 925.6322; found: 925.6310

Compound 4:

Pale yellow solid

mp: 147-148 °C

¹H NMR (300 MHz, CDCl₃-DMSO-*d*₆) δ: 8.16 (s, 2H), 7.89 (m, part of AA'BB', 2H), 7.36 (m, part of AA'BB', 2H), 7.16 (s, 2H), 4.09 (m, 4H), 4.04 (m, 2H), 3.96 (m, 2H), 3.71 (m, 2H), 3.38 (2H, bs), 2.14 – 1.21 (br. m, 52H, steroidal CH, CH₂), 1.14 (d, J = 6 Hz, 6H), 0.80 (s, 6H), 0.67 (s, 6H).

¹³C NMR (75 MHz, CDCl₃-DMSO-*d*₆) δ: 150.06, 130.12, 127.53, 126.34, 122.84, 121.45, 104.14, 72.19, 71.07, 67.42, 59.60, 47.03, 46.072, 41.39, 41.34, 39.46, 38.63, 35.12, 34.52, 34.42, 32.56, 30.20, 29.22, 28.09, 27.37, 26.07, 22.87, 22.28, 17.53, 12.22.

IR (KBr): 3260, 2921, 2854, 1576, 1462, 1190, 1078.

[α]_D²⁵ -6.6 (1, EtOH)

HRMS: Calcd. for C₆₀H₈₆O₈Na: 957.6220; found: 957.6296

Gelation test

A measured amount of gelator was weighed with the required amount of TNF and the mixture was heated after adding an appropriate amount of an organic solvent till a clear solution was formed. The solution was allowed to cool to room temperature. Gel formation was observed in a matter of 5-6 min.

Thermal stability studies

The gel to sol melting temperature (T_{gel}) was recorded by inverted test tube method. Gels (gel volume 0.3 mL) were prepared in the test tubes (10 mm x 75 mm), which were sealed and fixed upside down in an oil bath to measure the gel transition temperature by heating in an oil bath at a uniform rate of 2 °C/min.

All the CT gels were made with 1:1 ratio of donor and TNF for the comparison of T_{gel} values in different solvents. For the thermal stability studies all the CT gels were stabilized for 12-14 h at room temperature.

Variable temperature emission study

300 μL of the gel which had 2.7 mM each of the donor and the acceptor in *n*-octanol was prepared. The gel was heated and the sol was transferred into a 2 mm square quartz cuvette. The sol was allowed to gel at room temperature, following which the emission spectrum was recorded with increase in temperature. The temperature was varied from 20 °C to 80 °C and the spectra were recorded at 5 °C intervals (at each temperature, the gel was stabilized for 10 min).

Absorption and Emission Spectra of Charge transfer gel of 3/TNF

Absorption study was carried out in a 2 mm path length quartz rectangular cuvette. 400 μL of the gel was transferred as a hot sol into the cuvette and spectra were recorded.

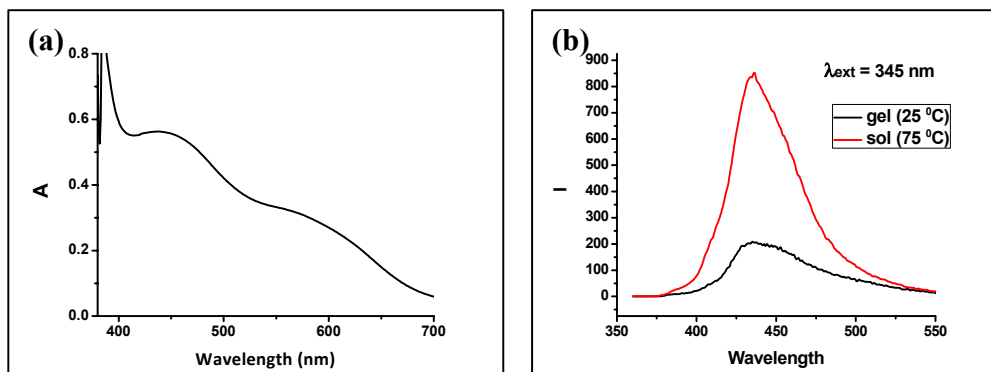


Fig S1 (a) Charge transfer band for 3/TNF (1:1 ratio) in *n*-octanol (donor concentration \approx 3.32 mM); (b) Emission spectra of the same in gel and sol states (slit widths 5/5 nm)

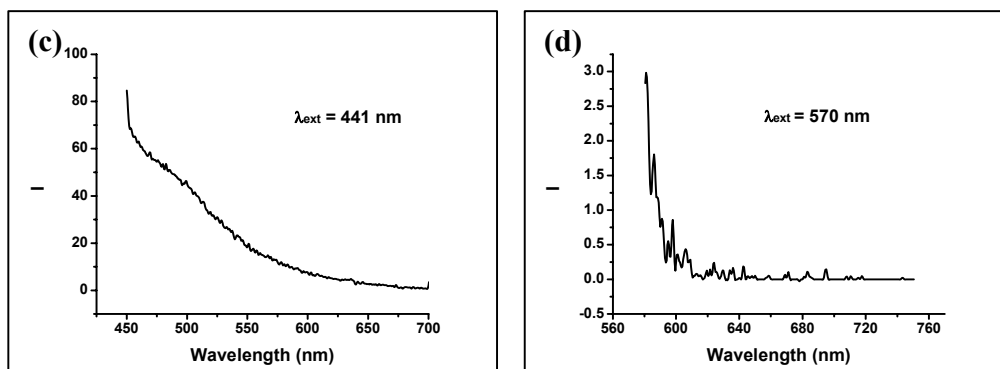


Fig S1 Emission spectra of CT gel of 3/TNF (1:1 ratio) in *n*-octanol (donor concentration \approx 3.32 mM) at two different wavelengths

Rheology

Dynamic rheological experiments were performed on the CT gels on an AR 1000 rheometer (TA Instruments) using plate-plate (hatched) geometry (20 mm diameter, 400 μm gap). The temperature of the plate was maintained at 25 $^{\circ}\text{C}$ (± 0.1 $^{\circ}\text{C}$). Hot sols were prepared and quickly transferred on to the stage by pre-heated Pasteur pipettes. The gels were stabilized for 5 min before the geometry was set. Experiments were initiated after the gels were stabilized under the geometry for 1 h.

Scanning Electron Microscopy

Hot sol was prepared and around 20-40 μL of the sol was placed on the carbon tape of SEM holders. Initially the gels were allowed to air dry for 12-14 h then were dried under high vacuum for 3-4 h.

References

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2. N. M. Sangeetha, R. Balasubramanian, U. Maitra, S. Ghosh and A. R. Raju, *Langmuir*, 2002, **18**, 7154.