Fluorescent ‘two-faced’ polymer wafers with embedded pyrene-functionalised gelator nanofibres

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1. **Synthetic Scheme, Methods and Characterisation Data**

![Chemical structure of the gelator G1-Py](image)

**Scheme S1.** Synthesis of gelator G1-Py.

**Compound 1**

L-Lysine methyl ester dihydrochloride¹ (1.03 g, 4.30 mmol) was suspended in dichloromethane (40 ml). NEt₃ (1.26 ml, 8.93 mmol) was added, followed by 1-pyrene butyric acid (1.45 g, 5.0 mmol). The mixture was stirred under a nitrogen atmosphere for 5 min. The mixture was cooled to 0°C, then HOBt (1.21 g, 8.93 mmol) and DCC (1.84 g, 8.93 mmol) were added simultaneously as a mixture of solids. The reaction was allowed to return to room temperature and stirred for 16 h. The precipitate was removed by filtration and washed with DCM (50 ml) followed by MeOH (100 ml) to leave the pure product as a beige solid with a yield of 2.60 g (86% yield). Rf: 0.67 (CH₂Cl₂:MeOH 90:10), Melting Point: 133-135°C, αD<sup>293</sup> +4.0 (c=1, CH₂Cl₂), δ<sub>H</sub> (400 MHz, CDCl₃) 7.50-7.21 (18H, m, ArH), 7.06-7.03 (4H, t, J = 8.0, CH₂Ar), 5.78 (1H, d, J = 7.6, CONH), 5.20 (1H, t, J = 5.5, CONH), 3.84 (1H, m, COCHR), 2.59 (4H, m, NHCOC₂H₂), 2.56 (2H, m, CONHCH₂), 1.57-0.54 (10H, m,
\[ CH_2 \], \( \delta_C \) (400 MHz, CDCl\(_3\)) 173.8 (CO\(_2\)Me), 173.3 (CONH), 173.2 (CONH), 132.7, 130.7, 130.2, 130.0, 127.8, 127.4, 127.3, 127.0, 126.2, 126.2, 125.1, 125.0, 124.4, 123.9, 123.5, 123.0 (all pyrene), 52.5 (COCHR), 51.7 (CO\(_2\)CH\(_3\)), 38.9 (CH\(_2\)NH), 36.8, 33.9, 31.9, 29.3, 26.2, 22.7 (all CH\(_2\)), \( \nu_{\max} \) (solid phase) 3319m (NH), 2928m, 2850m (CH\(_3\), CH\(_2\)), 1754m (COOCH\(_3\)), 1627s(CONH), 1538s (CONH), \( m/z \) (ESI) C\(_{47}\)H\(_{44}\)N\(_2\)O\(_4\) [M] requires 700.9; found 723.4 (100%, [M+Na]\(^+\)), 724.4 (45%), 701.3 (11% [M+H]\(^+\)), HR-ES requires 700.8633, found; 700.8633.

**Compound 2**

The methyl ester protected head group (1) (1.00 g, 1.43 mmol) was suspended in ethanol (50 ml) and potassium hydroxide (1.00 g, 1.78 mmol) added. The mixture was refluxed at 95°C overnight. The solvent was removed by rotary evaporation and water (50 ml) added. The aqueous solution was acidified to pH 3 using an aqueous HCl (10%). The product was extracted with EtOAc and washed with water and brine. The solution was then dried over sodium sulfate and rotary evaporated to dryness to yield a beige solid, 0.8 g (82%). \( R_f \): 0.24 (CH\(_2\)Cl\(_2\):MeOH 90:10), Melting Point: 136-138°C, \( \alpha_D^{293} \): +7.9, \( \delta_H \) (400 MHz, CDCl\(_3\)) 7.30-7.24 (18H, m, ArH), 7.00-6.98 (4H, m, CH\(_2\)Ar), 6.11 (1H, d, \( J = 7.04 \), CONH), 4.91 (1H, t, \( J = 5.8 \), CONH), 3.83 (1H, m, COCHR), 2.50 (4H, m, NHCOCH\(_2\)), 2.36 (2H, m, CH\(_2\)NHCO), 1.60-0.58 (10H, m, CH\(_2\)), \( \delta_C \) (400 MHz, CDCl\(_3\)) 174.6 (CO\(_2\)H), 173.1 (CONH), 173.1 (CONH), 132.7, 130.6, 130.1, 129.9, 127.8, 127.2, 127.0, 126.8, 126.2, 126.2, 125.2, 125.1, 124.4, 123.7, 123.5, 123.2 (all pyrene), 53.1 (COCHR), 51.6 (CO\(_2\)CH\(_3\)), 38.9 (CH\(_2\)NH), 37.0, 34.2, 32.6, 29.8, 26.4, 23.3 (all CH\(_2\)), \( \nu_{\max} \) (solid phase) 3293m (NH), 2933m, 2852m (CH\(_3\), CH\(_2\)), 1637m (CONH), 1586m (COOH), 1542m (CONH), \( m/z \) (ESI) C\(_{46}\)H\(_{42}\)N\(_2\)O\(_4\) [M] requires 686.8; found 685.3 (100%, [M-H]\(^-\)), 686.3 (47%), HR-ES requires 686.8367, found; 686.8370.

**Gelator G1-Py**

1,12-Diaminododecane (0.02 g, 0.10 mmol) was suspended in DCM (10ml). NEt\(_3\) (0.03 ml, 0.22 mmol) was added, followed by compound 2 (0.15 g, 0.22 mmol) and O-(7-azabenzotriazole-1-yl)-N,N,N’,N’-tetramethyluronium hexafluorophosphate...
(HATU, 0.084 g, 0.22 mmol) and the reaction mixture stirred under nitrogen for 24 h. The precipitate was removed by filtration and washed repeatedly with DCM to obtain the pure product as a beige solid, 0.11 g (65%) \( R_f 0.80 \) (CH\(_2\)Cl\(_2\):MeOH 90:10), Melting Point: decomposes >180°C, \( \alpha_D^{293} -14.0 \) (c=1, DMSO), \( \delta_H \) (400 MHz, DMSO-D6) 8.33-7.85 (42H, m, ArH and CONH), 7.82-7.80 (8H, m, CH\(_2\)Ar), 4.26-4.21 (2H, m, COCHR), 3.24-3.19 (8H, m, NHCOC\(_2\)), 3.05-3.03 (4H, m, CH\(_2\)NHCO), 3.01-2.95 (4H, m, CH\(_2\)NHCO), 2.29-2.27 (8H, m, NHCOC\(_2\)), 2.20-2.18 (4H, m, CONHCH\(_2\)), 1.65-0.65 (28H, m, CH\(_2\)). Low solubility hampered attempts to determine \(^{13}\)C NMR spectra, \( m/z \) (ESI) \( C_{104}H_{108}N_6O_6 \) [M] requires 1538; found 1561 (100%, [M+Na]\(^+\)), 1562 (48%), 1583 (14%), HR-ES requires 1538.0069, found; 1538.0072

2 Experimental Procedures

2.1 Procedure for Making Gels

An accurately measured mass of gelator was weighed out into a 2 ml glass vial. The solvent (1 ml) was then added using a Gilson pipette. The sample was sonicated for 30 minutes and heated with a heat gun until a homogeneous solution had been obtained which was then left to cool down. All gels were left over night to set.

2.2 Procedure for the Measurement of \( T_{gel} \) Values

Gel-sol transition temperatures (\( T_{gel} \)) were determined using the tube-inversion methodology, and represents the point at which the stress exerted by the gel exceeds its yield strength. All gel samples were prepared with a volume of 1 ml in vials with a diameter of 8 mm; this ensures that the stress generated by the tube inversion is constant in each case. The gels were then heated in an accurate temperature regulated oil bath at a rate of 1°C min\(^{-1}\), until solvent was observed to leach from the inverted gel. All \( T_{gel} \) values reported are based on an average of at least three replicate measurements.
2.3 Procedure for the Preparation of SEM Samples

A small amount of gel sample was removed from its glass vial with a spatula and it was spread thinly onto an aluminum stub and left to dry overnight under ambient conditions in a fume hood. Before imaging, the sample was covered in a thin layer (4 nm) of Pd/Pt using an Agar sputter coater before being placed in the microscope. In the case of the polymer wafers, these were fractured prior to imaging.

2.4 Procedure for Gel Polymerisation

Polymerisations were carried out using a 400 W UV flood lamp manufactured by UV Light Ltd. 5 ml samples were irradiated for 1 h in a glass template (500 x 20 x 8 mm) which was cooled by flowing water. All polymerisations were carried out in an atmosphere of nitrogen. Polymerisation of the styrene/DVB solvent in this gel was then achieved using UV initiation, at wavelengths >300 nm, with 4,4’-bis (dimethylamino)benzophenone as sensitizer.

3 Thermal Stability of Gel

Fig. S1. Thermal stability of gel determined in DMSO/styrene/DVB (1:8.2:0.8) at a range of concentrations.
4 Fluorescence Spectroscopic Data

Fig. S2. Emission spectra of G1-Py in DMSO/styrene/DVB (1:8.2:0.8) at concentrations of 0 M (cyan), $1 \times 10^{-5}$ M (yellow), $2.5 \times 10^{-5}$ M (magenta) and $5 \times 10^{-5}$ M (blue). Excitation wavelength is 343 nm.

Fig. S3. Emission spectra of G1-Py in DMSO at concentrations of 0 M (cyan), $1 \times 10^{-5}$ M (yellow), $2.5 \times 10^{-5}$ M (magenta), $5 \times 10^{-5}$ M (blue), $7.5 \times 10^{-5}$ (green) and $1 \times 10^{-4}$ (red). Excitation wavelength is 343 nm.
**Fig. S4.** Concentration dependence of the emission intensity of G1-Py in different solvent systems, indicating how gelator aggregation in DMSO/styrene/DVB leads to enhanced excimer emission followed by self-quenching of the fluorescence intensity. Excitation wavelength is 343 nm.

**Fig. S5.** Fluorescence spectra of G1-Py at the lower face of a polymer wafer containing poly(styrene/DVB) and DMSO at temperatures of 20°C (blue), 40°C (magenta), 60°C (yellow) and 80°C (cyan) demonstrating change in relative intensity of monomer and excimer emission bands. Excitation wavelength is 343 nm.
5    SEM Imaging

![SEM image of the roughened lower face of the polymer wafer after washing with THF and methanol removed some of the DMSO-rich portion of the material.](image)

**Fig. S6.** SEM image of the roughened lower face of the polymer wafer after washing with THF and methanol removed some of the DMSO-rich portion of the material.

6   Representative Elemental Analysis Data

**Table 5.1.** Nitrogen and sulfur content of polymer wafers pre- and post-wash. Nitrogen content reflects gelator loading, as the only nitrogen is associated with gelator molecules, sulfur content represents DMSO loading, as the only sulfur atoms are in the solvent.

<table>
<thead>
<tr>
<th>Gelator</th>
<th>N-content pre-wash / %</th>
<th>N-content post-wash / %</th>
<th>S-content pre-wash / %</th>
<th>S-content post-wash / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1-Py</td>
<td>0.73</td>
<td>0.61</td>
<td>3.46</td>
<td>1.31</td>
</tr>
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</table>

7   References