

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

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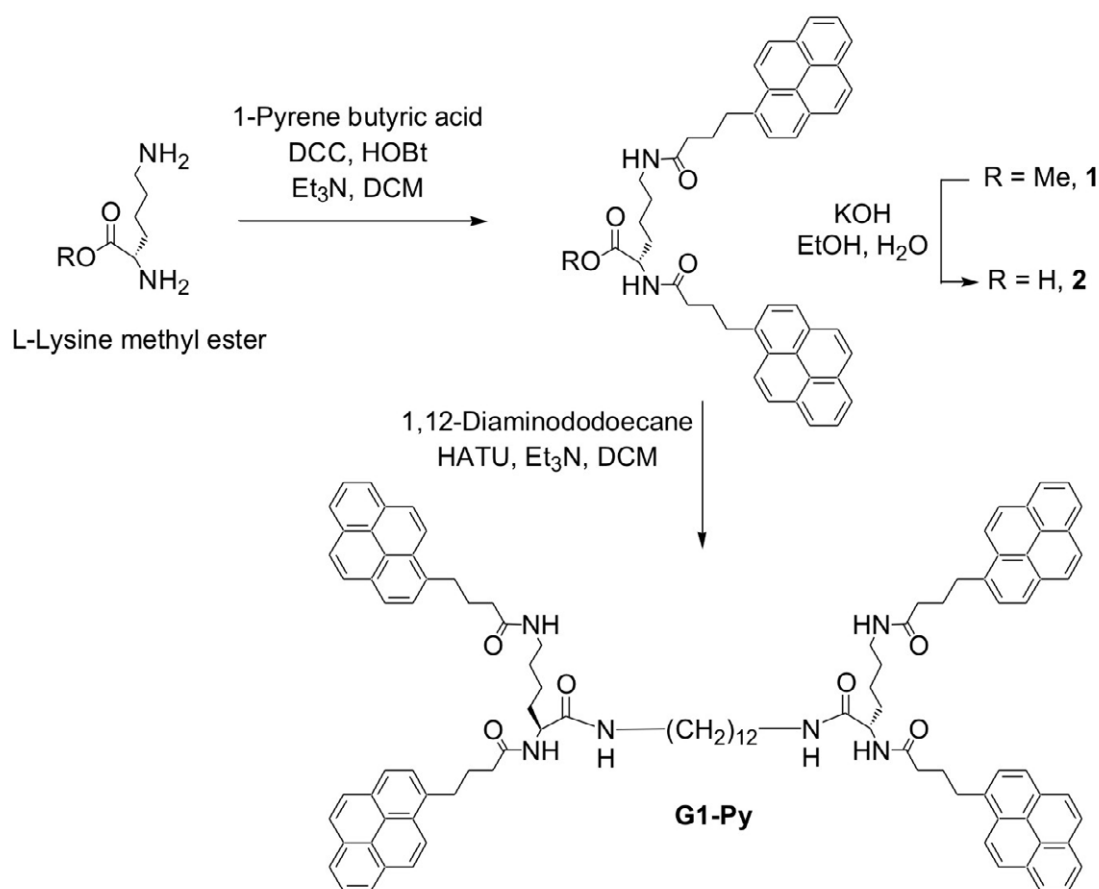
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SUPPLEMENTARY INFORMATION

Contents

- 1 Synthetic Scheme, Methods and Characterisation Data
- 2 Experimental Procedures
 - 2.1 Procedure for Making Gels
 - 2.2 Procedure for the measurement of T_{gel} values
 - 2.3 Procedure for the preparation of SEM samples
 - 2.4 Procedure for Gel Polymerisation
- 3 Thermal Stability of Gel
- 4 Fluorescence Spectroscopic Data
- 5 SEM Imaging
- 6 Representative Elemental Analysis Data
- 7 References

1. Synthetic Scheme, Methods and Characterisation Data



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). *R*_f: 0.67 (CH₂Cl₂:MeOH 90:10), Melting Point: 133-135°C, α_D²⁹³ +4.0 (c=1, CH₂Cl₂), δ_H (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, NHCOCH₂), 2.56 (2H, m, CONHCH₂), 1.57-0.54 (10H, m,

CH_2), δ_C (400 MHz, $CDCl_3$) 173.8 (CO_2Me), 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_2CH_3), 38.9 (CH_2NH), 36.8, 33.9, 31.9, 29.3, 26.2, 22.7 (all CH_2), ν_{max} (solid phase) 3319m (NH), 2928m, 2850m (CH_3 , CH_2), 1754m ($COOCH_3$), 1627s(CONH), 1538s (CONH), m/z (ESI) $C_{47}H_{44}N_2O_4$ [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_2Cl_2 :MeOH 90:10), Melting Point: 136-138°C, α_D^{293} : +7.9, δ_H (400 MHz, $CDCl_3$) 7.30-7.24 (18H, m, ArH), 7.00-6.98 (4H, m, CH_2Ar), 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_2NHCO), 1.60-0.58 (10H, m, CH_2), δ_C (400 MHz, $CDCl_3$) 174.6 (CO_2H), 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_2CH_3), 38.9 (CH_2NH), 37.0, 34.2, 32.6, 29.8, 26.4, 23.3 (all CH_2), ν_{max} (solid phase) 3293m (NH), 2933m, 2852m (CH_3 , CH_2), 1637m (CONH), 1586m (COOH), 1542m (CONH), m/z (ESI) $C_{46}H_{42}N_2O_4$ [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 (CH₂Cl₂:MeOH 90:10), Melting Point: decomposes >180°C, α_D^{293} : -14.0 (c=1, DMSO), δ_H (400 MHz, DMSO-D₆) 8.33-7.85 (42H, m, ArH and CONH), 7.82-7.80 (8H, m, CH₂Ar), 4.26-4.21 (2H, m, COCHR), 3.24-3.19 (8H, m, NHCOCH₂), 3.05-3.03 (4H, m, CH₂NHCO), 3.01-2.95 (4H, m, CH₂NHCO), 2.29-2.27 (8H, m, NHCOCH₂), 2.20-2.18 (4H, m, CONHCH₂), 1.65-0.65 (28H, m, CH₂). Low solubility hampered attempts to determine ¹³C NMR spectra, m/z (ESI) C₁₀₄H₁₀₈N₆O₆ [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

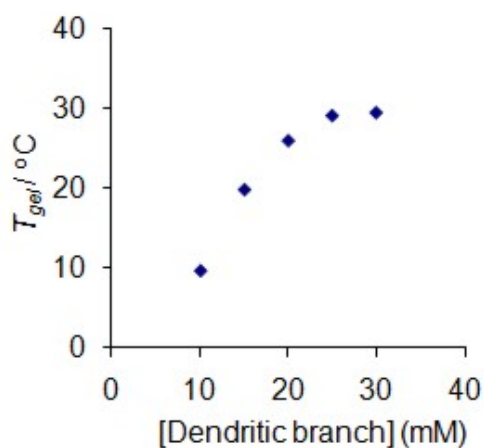


Fig. S1. Thermal stability of gel determined in DMSO/styrene/DVB (1:8.2:0.8) at a range of concentrations.

4 Fluorescence Spectroscopic Data

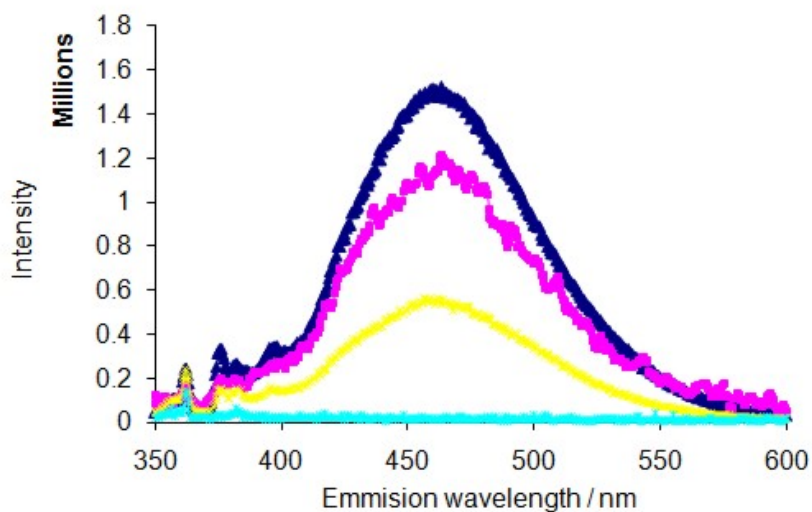


Fig. S2. Emission spectra of **G1-Py** in DMSO/styrene/DVB (1:8.2:0.8) at concentrations of 0 M (cyan), 1×10^{-5} M (yellow), 2.5×10^{-5} M (magenta) and 5×10^{-5} M (blue). Excitation wavelength is 343 nm.

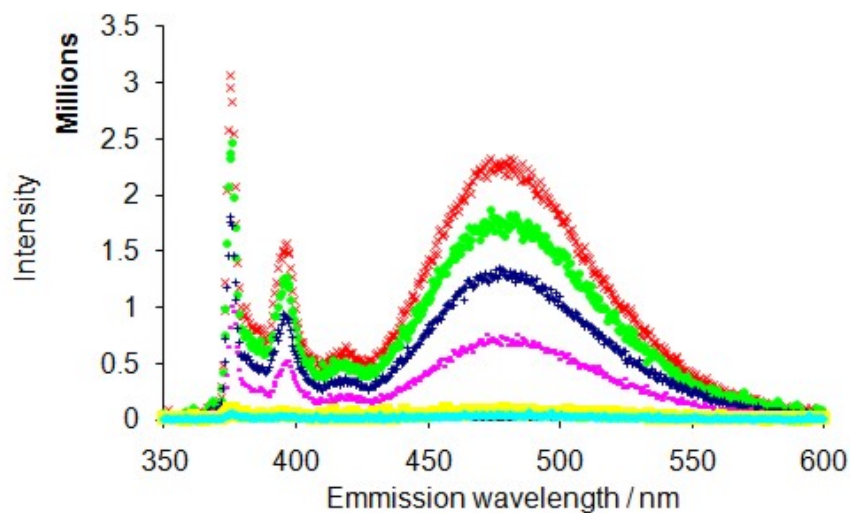


Fig. S3. Emission spectra of **G1-Py** in DMSO at concentrations of 0 M (cyan), 1×10^{-5} M (yellow), 2.5×10^{-5} M (magenta), 5×10^{-5} M (blue), 7.5×10^{-5} (green) and 1×10^{-4} (red).. Excitation wavelength is 343 nm.

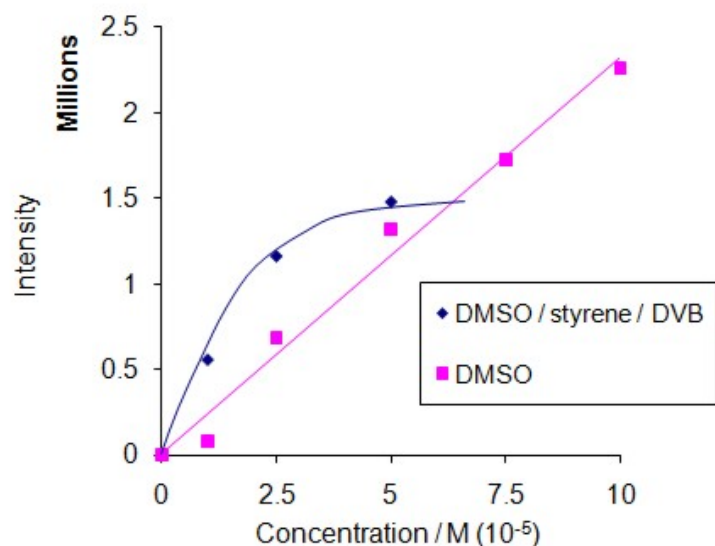


Fig. S4. Concentration dependence of the emission intensity of **G1-Py** in different solvent systems, indicating how gelator aggregation in DMSO/styrene/DVB leads to enhanced excimer emission followed by self-quenching of the fluorescence intensity. Excitation wavelength is 343 nm.

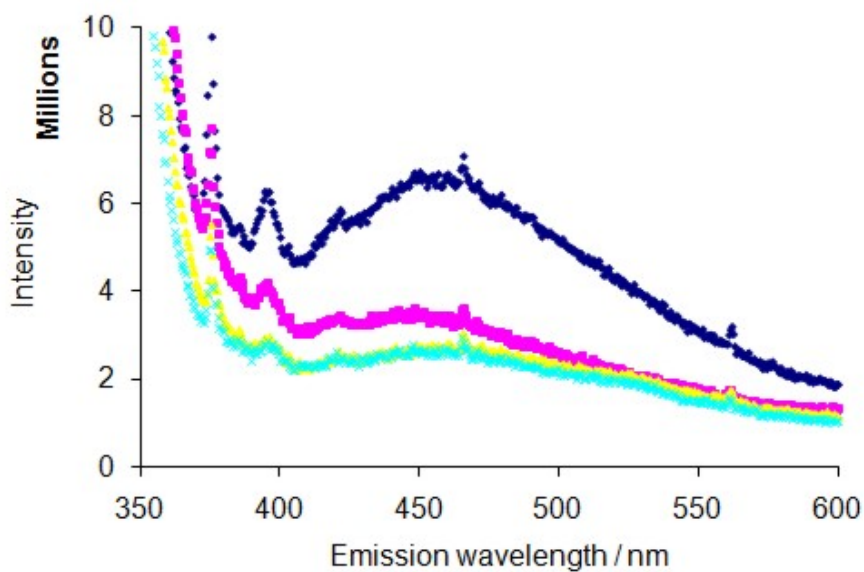


Fig. S5. Fluorescence spectra of **G1-Py** at the lower face of a polymer wafer containing poly(styrene/DVB) and DMSO at temperatures of 20°C (blue), 40°C (magenta), 60°C (yellow) and 80°C (cyan) demonstrating change in relative intensity of monomer and excimer emission bands. Excitation wavelength is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

5 SEM Imaging

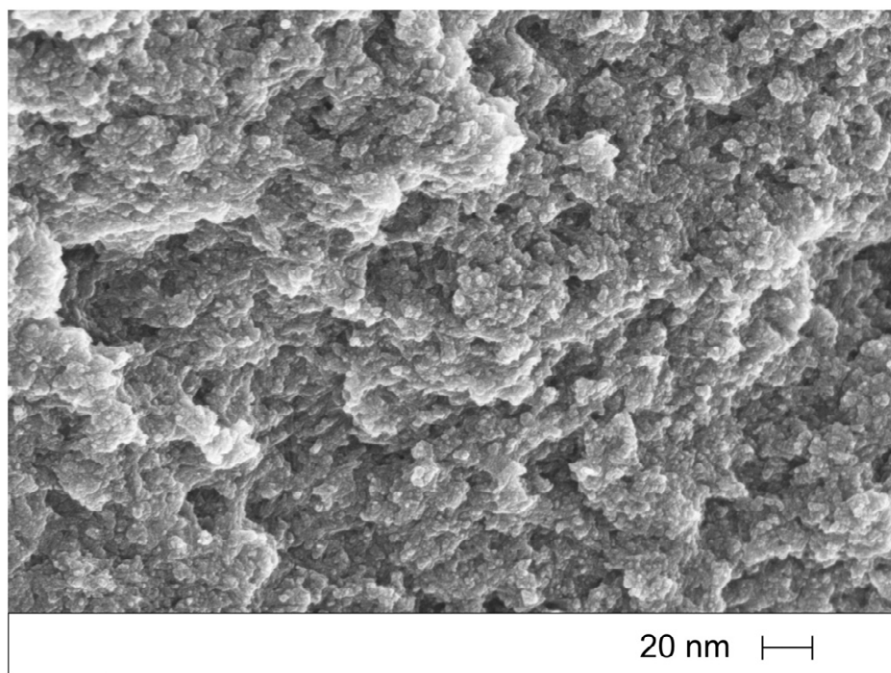


Fig. S6. SEM image of the roughened lower face of the polymer wafer after washing with THF and methanol removed some of the DMSO-rich portion of the material.

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.

Gelator	N-content pre-wash / %	N-content post-wash / %	S-content pre-wash / %	S-content post-wash / %
G1-Py	0.73	0.61	3.46	1.31

7 References

- 1 C. E. Davies, T. D. Heightman, S. A. Hermitage, M. G. Moloney, *Synth. Commun.*, **1996**, 26, 687-696