

## Dipeptide Hydrogelation Triggered via Ultraviolet Light

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### Supporting Information

#### Experimental Details

##### Materials

All dipeptide materials except 7MeOFF were prepared as described previously.<sup>1, 2</sup> Deionised water was used throughout. All other chemicals were purchased from Sigma-Aldrich and used as received. The PAG, diphenyliodonium nitrate (DPIN), was also purchased from Sigma-Aldrich and has reported  $\lambda_{\text{max}}$  values of 203 and 226 nm.

7MeOFF was prepared using an analogous synthetic procedure to that reported previously<sup>2</sup> from 7-methoxy-2-naphthol.

**Tert-butyl 2-(7-methoxynaphthalen-2-yloxy)acetate:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.67 (d, ArH, 1H, J<sub>HH</sub> = 6.7 Hz), 7.65 (d, ArH, 1H, J<sub>HH</sub> = 7.5 Hz), 7.06 (dd, ArH, 1H, J<sub>HH</sub> = 8.9 Hz, J<sub>HH</sub> = 2.5 Hz), 7.00 (m, ArH, 3H), 4.61 (s, OCH<sub>2</sub>, 2H), 3.89 (s, OCH<sub>3</sub>, 3H), 1.50 (s, CH<sub>3</sub>, 9H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 168.0, 158.3, 156.5, 135.7, 129.4, 129.2, 124.7, 116.4, 115.9, 106.6, 105.3, 52.4, 65.8, 55.3, 28.1 ppm. MS (ES) 311 ([M+Na]<sup>+</sup>). Accurate mass calculated for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>Na: 311.1259. Found: 311.1259.

**2-(7-Methoxynaphthalen-2-yloxy)acetic acid:** <sup>1</sup>H NMR (DMSO) 7.74 (d, ArH, 1H, J<sub>HH</sub> = 8.8Hz), 7.73 (d, ArH, 1H, J<sub>HH</sub> = 8.8Hz), 7.20 (d, ArH, 1H, J<sub>HH</sub> = 2.3Hz), 7.16 (d, ArH, 1H, J<sub>HH</sub> = 2.3Hz), 7.01 (dd, ArH, 1H, J<sub>HH</sub> = 9.6Hz, J<sub>HH</sub> = 2.3Hz), 6.99 (dd, ArH, 1H, J<sub>HH</sub> = 9.6Hz, J<sub>HH</sub> = 2.3Hz), 4.77 (s, OCH<sub>2</sub>, 2H), 3.85 (s, OCH<sub>3</sub>, 3H) ppm. <sup>13</sup>C NMR (DMSO) 170.1, 157.7, 156.2, 135.5, 129.1, 128.9, 123.9, 116.1, 116.6, 106.4, 105.4, 64.4, 55.1 ppm. MS (CI) 250 ([M+NH<sub>4</sub>]<sup>+</sup>).

**Ethyl 2-(2-(2-(7-methoxynaphthalen-2-yloxy)acetamido)-3-phenylpropanamido)-3-phenylpropanoate:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.70 (d, ArH, 1H, J<sub>HH</sub> = 9.4 Hz), 7.68 (d, ArH, 1H, J<sub>HH</sub> = 9.4 Hz), 7.16 (m, ArH and NH, 9H), 7.04 (m, ArH, 2H), 6.98 (m, ArH, 4H), 6.38 (d,

NH, 1H,  $J_{\text{HH}} = 7.6$  Hz), 4.74 (m, CHNH, 2H), 4.53 (s, OCH<sub>2</sub>, 2H), 4.13 (m, CH<sub>2</sub>CH<sub>3</sub>, 2H), 3.91 (s, OCH<sub>3</sub>, 3H), 3.05 (m, CH<sub>2</sub>Ph, 4H), 1.21 (t, CH<sub>3</sub>, 3H,  $J_{\text{HH}} = 7.2$  Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 170.9, 169.9, 168.4, 158.4, 55.5, 135.9, 135.7, 135.6, 129.7, 129.3, 129.2, 129.1, 128.6, 128.5, 127.1, 124.9, 116.9, 15.4, 106.8, 105.4, 67.1, 55.3, 53.8, 53.3, 50.8, 37.8, 14.1 ppm. MS (ES)<sup>+</sup> 577 ([M+Na]<sup>+</sup>). Accurate mass calculated for C<sub>33</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>Na: 577.2315. Found: 577.2317.

### **2-(-2-(2-(7-Methoxynaphthalen-2-yloxy)acetamido)-3-phenylpropanamido)-3-**

**phenylpropanoic acid:** <sup>1</sup>H NMR (DMSO) 8.44 (d, NH, 1H,  $J_{\text{HH}} = 7.8$  Hz), 8.10 (d, NH, 1H,  $J_{\text{HH}} = 8.6$  Hz), 7.73 (d, ArH, 2H,  $J_{\text{HH}} = 8.9$ Hz), 7.16 (m, ArH, 12 H), 6.99 (m, ArH, 2H), 4.65 (m, CHNH, 1H), 4.51 (s, OCH<sub>2</sub>, 2H), 4.48 (m, CHNH, 1H), 3.86 (s, OCH<sub>3</sub>, 3H), 3.08 (dd, CHPh, 1H,  $J_{\text{HH}} = 14.0$  Hz,  $J_{\text{HH}} = 5.3$  Hz), 3.02 (dd, CHPh, 1H,  $J_{\text{HH}} = 14.0$  Hz,  $J_{\text{HH}} = 5.3$  Hz), 2.92 (dd, CHPh, 1H,  $J_{\text{HH}} = 14.0$  Hz,  $J_{\text{HH}} = 8.8$ Hz), 2.85 (dd, CHPh, 1H,  $J_{\text{HH}} = 14.0$  Hz,  $J_{\text{HH}} = 8.8$ Hz) ppm. <sup>13</sup>C NMR (DMSO) 172.7, 170.8, 167.2, 157.7, 156.0, 137.4, 137.3, 135.5, 129.2, 129.1, 128.9, 128.1, 127.9, 126.4, 126.4, 116.1, 115.6, 106.8, 105.4, 66.6, 55.1, 53.5, 53.2, 37.4, 36.6 ppm. MS (ES)<sup>-</sup> 525 ([M - H]<sup>-</sup>)

### **Sample Preparation**

A 0.5 wt% stock solution of dipeptide material at approximately pH 9 – 10 was prepared by adding dilute sodium hydroxide solution (1 molar equivalent of a 0.1 M solution) with stirring until fully dissolved. Stirring overnight was required for 7MeOFF, ~ 1 hour stirring for CNNapFF and 2NapFF; the other dipeptide materials dissolved within minutes of stirring. The PAG (1 molar equivalent) was added to this solution before leaving to stir overnight for the viscous solutions (7MeOFF, CNNapFF and 2NapFF) and less than 1 hour stirring was needed for complete dissolution in the other gelator solutions.

### **pH Measurements**

A calibrated FC200 pH probe (HANNA instruments) with a (6 mm x 10 mm) conical tip was used for the pH measurements and pK<sub>a</sub> titrations. The stated accuracy of the pH measurements is ±0.1. The pK<sub>a</sub> values of the dipeptide solutions were determined by titration at 25 °C via the addition of aliquots of a 0.1 M hydrochloric acid solution. To prevent gelation of the stock solution, gentle stirring was applied throughout. BrNapAV, CNNapFF and FmocLG were measured previously<sup>2</sup>.

### **UV Irradiation**

To form gels, samples were irradiated with UV light from a 40 W Spectroline X-series UV lamp (wavelength 254 nm). 2 mL of stock solution was placed in a 7 mL Sterilin cup and UV light was irradiated from above with the lid off the cup.

### **Rheological Measurements**

Rheological measurements were made on an Anton Paar Physica MCR101 rheometer. A cup and vane system was used which allowed the direct measurement of the gels formed in the 7 mL Sterilin cups. Frequency scans were performed from 1 rad s<sup>-1</sup> to 100 rad s<sup>-1</sup> under a strain of 0.5 %. The shear moduli (storage modulus  $G'$  and loss modulus  $G''$ ) were measured at a frequency of 10 rad s<sup>-1</sup>. All shear moduli measured were within the linear viscoelastic (LVE) region for the gels measured.

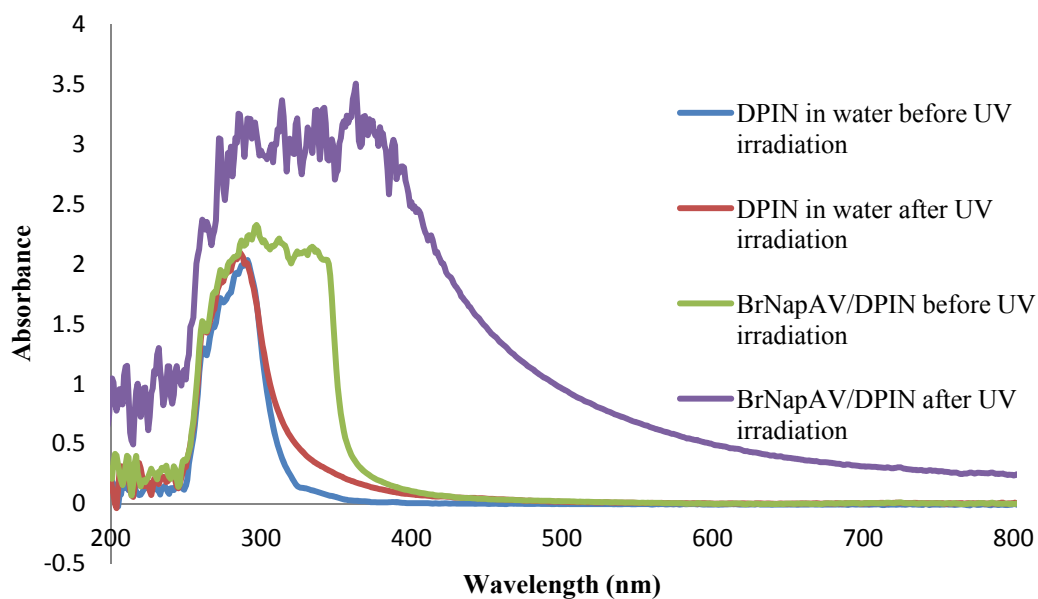
### **SEM**

Scanning electron microscopy images were recorded using a Hitachi S-4800 FE-SEM at 3 kV. Glass coverslips were stuck onto aluminium SEM stubs using carbon sticky tabs (Agar Scientific) and an aliquot of gel sample was then placed onto the surface of the glass (using a microspatula) and left to dry overnight. The samples were gold coated for 3 minutes at 15  $\mu$ A using a sputter-coater (EMITECH K550X) prior to imaging.

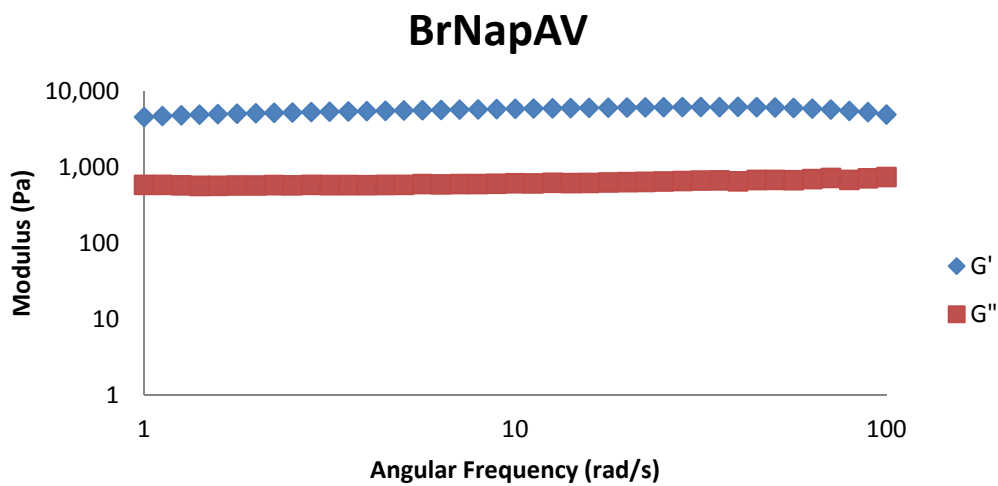
### **Hydrogel Patterning**

Gelator solutions with PAG were prepared as described above. Samples were then placed in quartz glass cuvettes. Part of the cuvette was covered with card stuck onto the cuvette to act as a UV mask. The sample was then irradiated using 2 half cylinder arrangements of 6 x 8 W Coast Wave backlit UV lamps for 3 – 4 hours. Once removed, the gel was photographed and the pH measured.

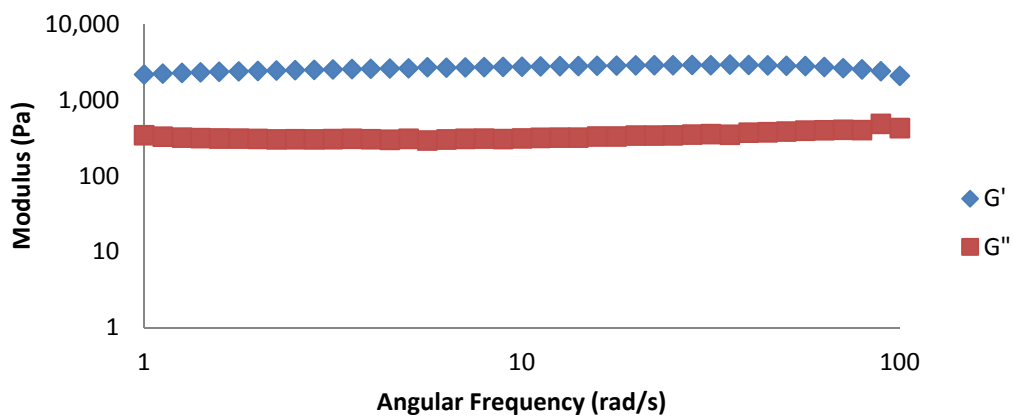
**Fig S1** – UV Spectrum of PAG in water



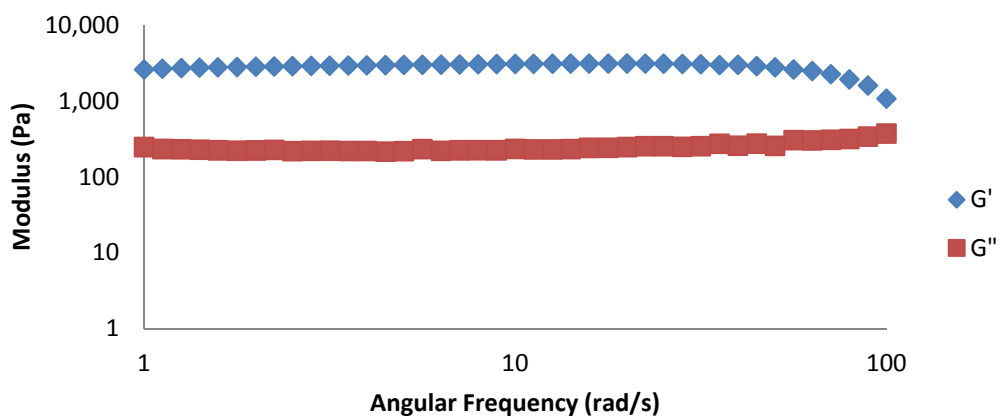
**Fig S2** – Rheological Properties of Gels Prepared Using PAG (Frequency Sweeps)



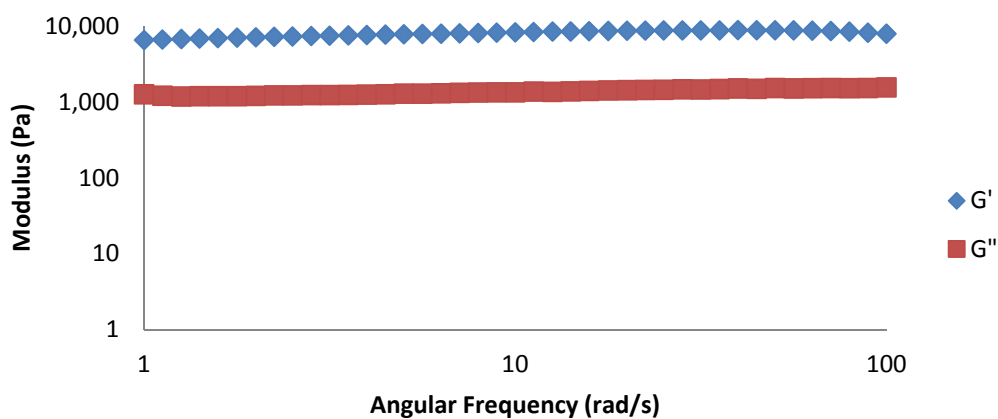
### CNNapFF



### 7MeOFF



### FmocLG



## **References**

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2. L. Chen, S. Revel, K. Morris, L. C. Serpell and D. J. Adams, *Langmuir*, 2010, 26, 13466-13471.