Electronic Supplementary Material (ESI) for Soft Matter.

Electrofabrication of large volume di- and tripeptide hydrogels via hydroquinone oxidation

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Supporting Information

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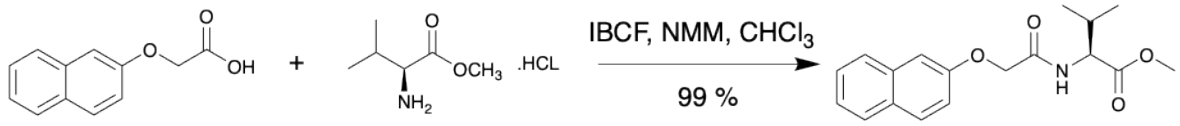
Experimental

1 Materials

All chemicals and solvents were purchased from Sigma Aldrich and used as received. 2NapAA[1] and 6Br2NapAV[1] and were synthesized as previously described. Full synthesis of 2NapVVV and 6Br2NapVF is reported in Section 1.1 and Section 1.2. Deionized Milli-Q water was used consistently throughout every experiment.

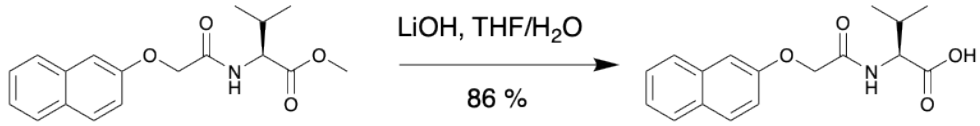
1.1 2NapVVV synthesis



Scheme S1. Synthesis of 2NapVOMe

To a suspension of 2-naphthoxyacetic acid (8.10 g, 40 mmol) in chloroform (100 mL) at 0 °C (ice-bath) were added *iso*-butyl chloroformate (1 eq, 5.18 mL) and *N*-methylmorpholine (1 eq, 4.40 mL) and the mixture was stirred for 20 minutes. A solution of L-valine methyl ester hydrochloride (1 eq, 6.71 g) and *N*-methylmorpholine (1 eq, 4.40 mL) in chloroform (100mL) was then added and the reaction was stirred overnight and allowed to warm to room temperature. After this time, the reaction mixture was diluted with chloroform and washed in turn with water (2×), 1M hydrochloric acid and brine. After drying over magnesium sulfate and evaporation *in vacuo*, the compound 2NapVOMe was obtained as a viscous orange oil (11.90 g, 99 %). This was used in the next step without further purification.

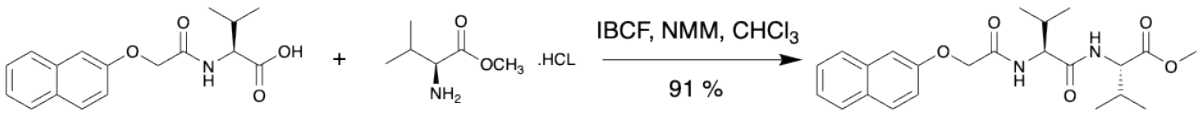
δH(400 MHz, DMSOd6): 8.39 (1H, d, *J* 8.3 Hz, N**H**), 7.87-7.22 (7H, m, **Aro**), 4.76 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$) 4.72 (1H, d, *J* 14.3 Hz, C$\mathbf{H}_2$), 4.29 (1H, dd, *J* 8.3, 6.4 Hz, *C**H**), 3.65 (3H, s, OC$\mathbf{H}_3$), 2.12 (1H, m, C**H**$(CH_3)_2$), 0.89 (6H, dd, *J* 6.7, 5.8 Hz, 2 X CH(C$\mathbf{H}_3)_2$). **δC (100 MHz, DMSO-d6):** 171.8, 167.9 (C=O), 155.7, 134.0, 129.3, 128.7, 127.5, 126.6, 126.5, 123.8, 118.6, 107.2 (CAr), 66.5 (CH_2), 57.1 (*CH), 51.7 (OCH_3), 29.8 (**C**H$(CH_3)_2$), 18.9, 18.1 CH(**C**$H_3)_2$). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{18}H_{21}NNaO_4$: 338.1364 Found: 338.1364.



Scheme S2. Deprotection of 2NapVOMe

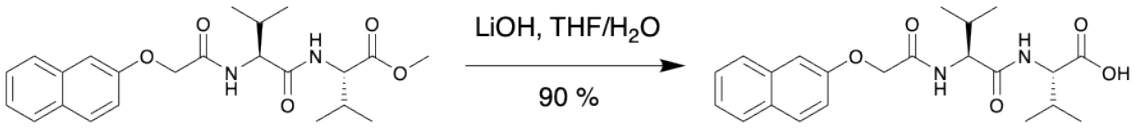
To a solution of 2NapVOMe (11.90 g, 39 mmol) in tetrahydrofuran (120 mL) was added a solution of lithium hydroxide (5 eq, 4.73 g) in water (120 mL) and was stirred vigorously for 30 minutes. The reaction was monitored using TLC (1:9 EtOAc:DCM). After this time, the TLC indicated the deprotection was complete. The reaction mixture was then poured into 1M hydrochloric acid (ca. 800 mL) and stirred for a further 20 minutes. The precipitate was filtered off, then washed with several portions of water. Drying by azeotropic distillation with acetonitrile on a rotary evaporator, followed by keeping at 40 °C under vacuum overnight, affording the compound 2NapVOH as a white solid (9.67 g, 86%). This was used in the next step without further purification.

δH(400 MHz, DMSOd6): 8.22 (1H, d, *J*, 8.6 Hz, N**H**), 8.14-7.24 (7H, m, **Aro**), 4.76 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$), 4.71 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$), 4.24 (1H, dd, *J* 8.6, 5.7 Hz,*C**H**), 2.12 (1H, m, C**H**$(CH_3)_2$), 0.89 (6H, dd, *J* 6.8, 5.7 Hz, 2 X CH(C$\mathbf{H}_3)_2$). **δC (100 MHz, DMSO-d6):** 172.7, 167.7 (C=O), 155.7, 134.0, 129.3, 128.7, 127.5, 126.6, 126.4, 123.8, 118.5, 107.2 (CAr), 66.6 (CH_2), 56.8 (*CH), 29.9 (**C**H$(CH_3)_2$), 19.1, 17.9 CH(**C**$H_3)_2$). **HRMS (ESI) m/z:** $[M+H]^+$ accurate mass calculated for $C_{17}H_{20}NO_4$: 302.1387. Found: 302.1390.



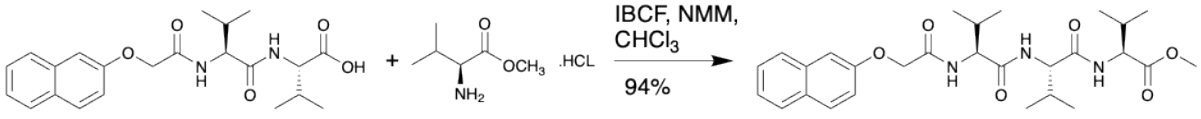
Scheme S3. Synthesis of 2NapVVOMe

To a suspension of 2NapVOH (9.67 g, 33.7 mmol) in chloroform (100 mL) was added *N*-methylmorpholine (1 eq, 3.70 mL) and the mixture was cooled in ice/water. Isobutyl chloroformate (1 eq, 4.37 mL) was added (upon which all solids dissolved) and the mixture was stirred for 15 minutes. A solution of L-valine methyl ester hydrochloride (1 eq, 5.65 g) and *N*-methylmorpholine (1 eq, 3.70 mL) in chloroform (60 mL) was then added and the reaction mixture was stirred at ambient temperature overnight. After this time, it was diluted with an approximately equal amount of chloroform, washed in turn with water (2×), 1M hydrochloric acid and brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The compound 2NapVVOMe was obtained as a pale-brown solid The product was purified by column chromatography using 1:9 EtOAc:DCM to give a white solid (12.73 g, 91%)
δH(400 MHz, DMSOd6): 8.21 (1H, d, *J* 8.4 Hz, N**H**), 7.94 (1H, d, *J* 8.7 Hz, N**H**), 7.90-7.19 (7H, m, **Aro**), 4.73 (1H, d, *J* 14.7 Hz, C**H**$_2$), 4.69 (1H, d, *J* 14.7 Hz, C**H**$_2$), 4.45 (1H, dd, *J* 8.7, 6.8 Hz,*C**H**), 4.13 (1H, dd, *J* 8.3, 5.9 Hz,*C**H**), 3.65 (3H, s, OC**H**$_3$), 2.12 (1H, m, C**H**(CH$_3$)$_2$), 1.97 (1H, m C**H**(CH$_3$)$_2$), 0.85 (12H, m, 2 X CH(C**H**$_3$)$_2$. **δC (100 MHz, DMSO-d6):** 171.7, 171.1, 167.2 (C=O), 155.5, 134.0, 129.4, 128.7, 127.5, 126.6, 126.4, 123.8, 118.9, 107.3 (CAr), 66.7 (CH$_2$), 57.6, 56.7 (*CH), 51.5 (O**C**H$_3$), 30.9, 29.6 (**C**H(CH$_3$)$_2$), 19.0, 18.8, 18.2, 17.9 CH(**C**H$_3$)$_2$). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{23}H_{30}N_2NaO_5$: 437.2047. Found: 437.2048.



Scheme S4. Deprotection of 2NapVVOMe

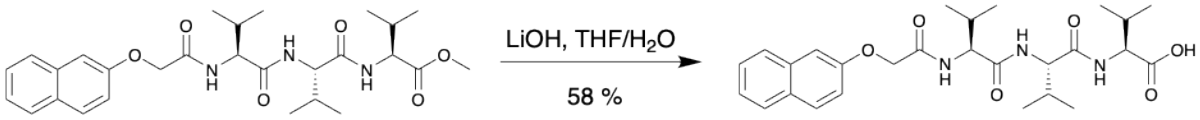
To a solution of 2NapVVOMe (12.73 g, 31 mmol) in tetrahydrofuran (120 mL) was added a solution of lithium hydroxide (5 eq, 3.68 g) in water (120 mL) and was stirred vigorously for 30 minutes. The reaction was monitored using TLC (1:9 EtOAc:DCM). After this time the TLC indicated the deprotection was complete. The reaction mixture was then poured into 1M hydrochloric acid (ca. 800 mL) and stirred for a further 20 minutes. The precipitate was filtered off, then washed with several portions of water. Drying by azeotropic distillation with acetonitrile on a rotary evaporator, followed by keeping at 40 °C under vacuum overnight, affording the compound 2NapVVOH as a white solid. (11.20 g, 90 %).
δH(400 MHz, DMSOd6): 12.57 (1H, s, O**H**), 8.13 (1H, d, *J* 8.1 Hz, N**H**), 7.9 (1H, d, *J* 9.0 Hz, N**H**), 7.87-7.21 (7H, m, **Aro**), 4.73 (1H, d, *J* 14.7 Hz, C**H**$_2$), 4.69 (1H, d, *J* 14.7 Hz, C**H**$_2$), 4.42 (1H, dd, *J* 9.0, 6.6 Hz,*C**H**), 4.11 (1H, dd, *J* 8.1, 5.9 Hz,*C**H**), 2.04 (1H, m, C**H**(CH$_3$)$_2$), 2.00 (1H, m C**H**(CH$_3$)$_2$), 0.85 (12H, m, 2 X CH(C**H**$_3$)$_2$. **δC (100 MHz, DMSO-d6):** 172.7, 171.0, 167.3 (C=O), 155.6, 134.0, 129.4, 128.7, 127.5, 126.6, 126.5, 123.8, 118.5, 107.3 (Car), 66.8 (CH$_2$), 57.4, 56.8 (*CH), 31.0, 29.6 (**C**H(CH$_3$)$_2$), 19.1, 19.0, 18.1, 17.9 CH(**C**H$_3$)$_2$). **HRMS (ESI) m/z:** $[M+H]^+$ accurate mass calculated for $C_{22}H_{29}N_2O_5$: 401.2071 Found: 401.2070.



Scheme S5. Synthesis of 2NapVVVOMe

To a suspension of 2NapVVOH (11.20 g, 28 mmol) in chloroform (120 mL) was added *N*-methylmorpholine (1 eq, 3.10 mL) and the mixture was cooled in ice/water. Isobutyl chloroformate (1 eq, 3.63 mL) was added (upon which all solids dissolved) and the mixture was stirred for 20 minutes. A solution of L-valine methyl ester hydrochloride (1 eq, 4.69 g) and *N*-methylmorpholine (1 eq, 3.10 mL) in chloroform (50 mL) was then added and the reaction mixture was stirred at ambient temperature overnight. After this time, it was diluted with an approximately equal amount of chloroform, washed in turn with water (2×), 1M hydrochloric acid and brine, dried (MgSO4), filtered, and evaporated under reduced pressure. The compound 2NapVVVOMe was obtained as a pale-brown solid (13.58 g, 94 % crude yield). This was used in the next step without further purification.

δH(400 MHz, DMSOd6): 8.12 (1H, d, *J* 7.7 Hz, N**H**), 7.83 (1H, d, *J* 7.9 Hz, N**H**), 7.75 (1H, d, *J* 8.2 Hz, N**H**), 8.04-7.21 (7H, m, **Aro**), 4.73 (1H, d, *J* 14.7 Hz, C$\mathbf{H}_2$) 4.68 (1H, d, *J* 14.7 Hz, C$\mathbf{H}_2$), 4.36 (1H, dd, *J* 8.9, 6.7 Hz, *C**H**), 4.26 (1H, dd, *J* 8.7, 7.4 Hz, *C**H**), 4.15 (1H, dd, *J* 7.8, 6.3 Hz, *C**H**), 3.61 (3H, s, OC$\mathbf{H}_3$), 1.99 (3H, m, 3 X C**H**$(CH_3)_2$), 0.84 (18H, m, 3 X CH$(CH_3)_2$). **δC (100 MHz, DMSO-d6):** 171.7, 171.1, 170.5, 167.3 (C=O), 155.5, 134.0, 129.4, 128.7, 127.5, 126.7, 126.4, 123.8, 118.5, 107.3 (Car), 66.7 (CH_2), 57.5, 57.4, 57.1 (*CH), 51.5 (O$\mathbf{C}H_3$), 30.8, 30.5, 29.6 (**C**H$(CH_3)_2$), 19.1 18.9, 18.8, 18.2, 18.1, 17.9 CH(**C**$H_3)_2$). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{28}H_{39}N_3NaO_6$: 536.2737. Found: 536.2741.



Scheme S6. Deprotection of 2NapVVVOMe

To a solution of 2NapVVVOMe (13.58 g, 26 mmol) in tetrahydrofuran (150 mL) was added a solution of lithium hydroxide (5 eq, 3.16 g) in water (150 mL) and was stirred vigorously for 30 minutes. The reaction was monitored using TLC (1:9 EtOAc:DCM). After this time, TLC indicated the deprotection was complete. The reaction mixture was then poured into 1M hydrochloric acid (ca. 800 mL) and stirred for a further 20 minutes. The precipitate was filtered off, then washed with several portions of water. Drying by azeotropic distillation with acetonitrile on a rotary evaporator, followed by keeping at 40 °C under vacuum overnight, affording the compound 2NapVVVOH as a light brown solid (11.20 g, 90 %). The ^{1}H NMR spectrum indicated the presence of an impurity and was recrystallised in acetonitrile to give the pure compound as a white solid (6.50 g, 58%).

δH(400 MHz, DMSOd6): 8.02 (1H, d, *J* 3.4 Hz, N**H**), 7.99 (1H, d, *J* 3.4 Hz, N**H**), 7.92 (1H, d, *J* 8.3 Hz, N**H**), 7.86-7.22 (m, 7H, **Aro**), 4.73 (1H, d, *J* 14.7 Hz, C$\mathbf{H_2}$), 4.68 (1H, d, *J* 15.16 Hz, C$\mathbf{H_2}$), 4.37 (1H, dd, *J* 8.9, 6.6 Hz, *C**H**), 4.3 (1H. dd, *J* 8.7, 7.3 Hz, *C**H**), 4.1 (1H, dd, *J* 8.2 Hz, 5.8 Hz, *C**H**), 1.99 (3H, m, 3 X C**H**$(CH_3)_2$), 0.84 (18H, m, 3 X CH$(CH_3)_2$). **δC (100 MHz, DMSO-d6):** 172.8, 171.1, 170.6, 167.3 (C=O), 155.6, 134.1, 129.4, 128.7, 127.5, 126.7, 126.4, 123.8, 118.5, 107.3 (C_{Ar}), 66.8 (CH_2) 57.6, 57.2, 57.2 (***C**H), 30.9, 30.5, 29.7 (**C**H$(CH_3)_2$), 19.2, 19.1, 19.0, 18.2, 17.9, 17.9 (CH(**C**$H_3)_2$). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{27}H_{37}N_3NaO_6$: 522.2575. Found: 522.2572.

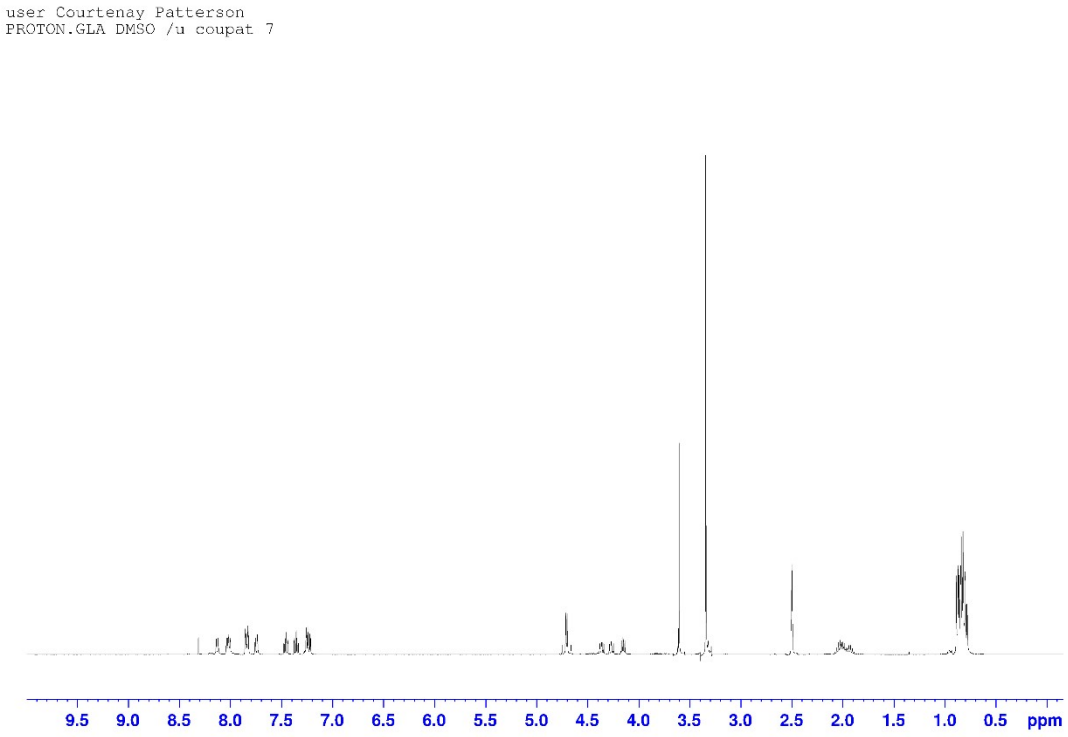
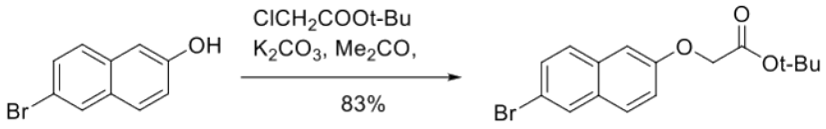


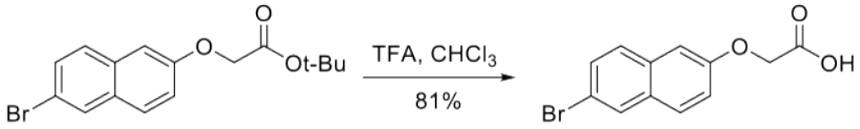
Figure S1. Proton NMR spectrum of 2NapVVVOH in d_6-DMSO.

1.2 6Br2NapVF Synthesis



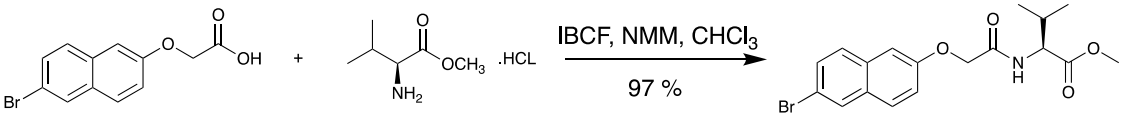
Scheme S7. Synthesis of 6Br2NapO^{t}Bu.
To a solution of 6-bromo-2-naphthol (11.50 g, 51.6 mmol) in acetone (130 mL) was added potassium carbonate (1 eq, 7.13 g) and the mixture was stirred overnight in a flask equipped with reflux condenser and $CaCl_2$ drying tube. After this time, *tert*-butyl chloroacetate (1.05 eq, 7.38 mL) and another portion of potassium carbonate (1 eq, 7.13 g) were added and the mixture was heated at reflux (70 °C oil bath temperature) overnight. After this time, TLC (5:95 ethyl acetate/*n*-hexane) appeared to indicate the absence of starting naphthol. The reaction mixture was evaporated to dryness under reduced pressure and the residue was partitioned between dichloromethane and water and stirred until all solids had dissolved. The layers were separated and the aqueous phase was extracted with dichloromethane. The combined organics were washed in turn with water, and brine, dried ($MgSO_4$), filtered and evaporated under reduced pressure, affording a dark brown oil (17.0 g). Proton NMR of this indicated the presence of a small amount of starting naphthol. Column chromatography (eluting with 4:6 dichloromethane/*n*-hexane, wet-loaded, 5×8 cm) afforded the title compound as a yellow oil which solidified on standing (14.50 g, 83 %). This was used in the next step without further purification. A small amount of an unidentified impurity is seen in the proton NMR around 4.25 ppm.
δH(400 MHz, DMSOd6): 8.12 (1H, d, *J* 1.88 Hz, $\underline{H}_{Ar}$), 7.85 (1H, d, *J* 9.00 Hz, $\underline{H}_{Ar}$), 7.76 (1H, d, *J* 8.84 Hz, $\underline{H}_{Ar}$), 7.57 (1H, dd, *J* 8.74, 2.06 Hz, $\underline{H}_{Ar}$), 7.29 (1H, d, *J* 2.48 Hz, $\underline{H}_{Ar}$), 7.25 (1H, dd, *J* 8.90, 2.58, Hz $\underline{H}_{Ar}$), 4.77 (2H, s, C$\underline{H}_2$), 1.43 (9H, s, C(C$\underline{H}_3$)$_3$). **δC (100 MHz, DMSO-d6):** (100 MHz, DMSO-

d_6) 167.5 (C=O), 155.9, 132.6, 129.8, 129.3, 129.3, 128.9, 128.7, 119.5, 116.5, and 107.3 (C_{Ar}), 81.4 ($C(CH_3)_3$), 65.1 (CH_2), 27.7 ($C(CH_3)_3$). **HRMS (ESI) m/z:** $[M]^+$ accurate mass calculated for $C_{16}H_{17}{}^{79}BrO_3$: 336.0361; found: 336.037.

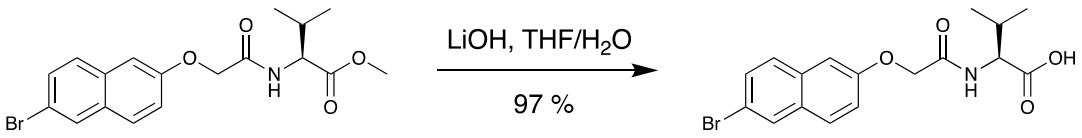


Scheme S8. Synthesis of 6Br2NapOH
To a solution of 6Br2NapOH (18.50 g, 55 mmol) in chloroform (80 mL) was added trifluoroacetic acid (*ca.* 10 eq, 42 mL) and the mixture was stirred overnight. After this time, it was poured into diethyl ether (500 mL), stirred for 1 hour, then filtered. The solid in the filter was washed with several portions of diethyl ether and dried under vacuum. The title compound was thus obtained as a white solid (12.50 g, 81%).

δH(400 MHz, DMSOd6): (400 MHz, DMSO-d_6) 13.11 (1H, br s, COOH), 8.12 (1H, d, *J* 1.92 Hz, H_{Ar}), 7.85 (1H, d, *J* 9.00 Hz, H_{Ar}), 7.77 (1H, d, *J* 8.80 Hz, H_{Ar}), 7.57 (1H, dd, *J* 8.76, 2.04 Hz, H_{Ar}), 7.32 (1H, d, *J* 2.48 Hz, H_{Ar}), 7.26 (1H, dd, *J* 8.96, 2.60 Hz, H_{Ar}), 4.80 (2H, s, OCH_2). **δC (100 MHz, DMSO-d6):** (100 MHz, DMSO-d_6) 170.0 (C=O), 156.1, 132.7, 129.9, 129.4, 129.3, 129.0, 128.7, 119.6, 116.5, and 107.2 (C_{Ar}), 64.6 (OCH_2). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{12}H_9{}^{79}BrNaO_3$ 302.9627. found 302.9629.

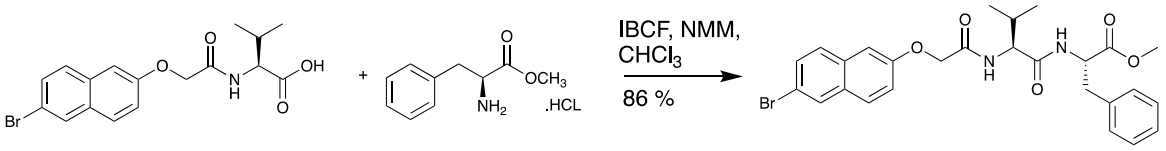


Scheme S9. Synthesis of 6Br2NapVOme
To a solution of 6Br2NapOH (5.40 g, 19 mmol) in chloroform (60 mL) was added isobutyl chloroformate (1 eq, 2.46 mL) followed by *N*-methylmorpholine (1 eq, 2.10 mL). After 10 minutes, L-valine methyl ester hydrochloride (1 eq, 3.18 g) and another portion of *N*-methylmorpholine (1 eq, 2.10 mL) were added and the reaction was stirred overnight. It was then diluted with chloroform, washed water (2×), 1M hydrochloric acid and brine, dried (MgSO4), filtered, and evaporated under reduced pressure. The resulting white solid (7.30 g, 97%) was used directly in the next step.
δH(400 MHz, DMSOd6): 8.41 (1H, d, *J* 8.3 Hz, N**H**), 7.85 (1H, d, *J* 8.8 Hz, N**H**), 8.13-7.24 (6H, m, **Aro**), 4.76 (1H, d, *J* 14.4 Hz, C**H**$_2$), 4.71 (1H, d, *J* 14.6 Hz, C**H**$_2$), 4.26 (1H, dd, *J* 8.3, 6.4 Hz, ***CH**), 3.64 (3H, s, OC**H**$_3$), 2.11 (1H, m, C**H**$(CH_3)_2$), 0.89 (6H, dd, J 6.7, 5.3 Hz, CH(C**H**$_3)_2$). **δC (100 MHz, DMSO-d6):** (100 MHz, DMSO-d_6) 167.4, 169.8 (C=O), 156.3, 132.7, 129.8, 129.4, 129.1, 129.0, 128.6, 119.6, 116.5, 107.3 (C_{Ar}), 65.0 (CH_2), 56.3 (*CH), 50.4 (OCH_3), 28.3 **C**H(CH_3),18.8, 18.3 CH(**C**$H_3)_2$



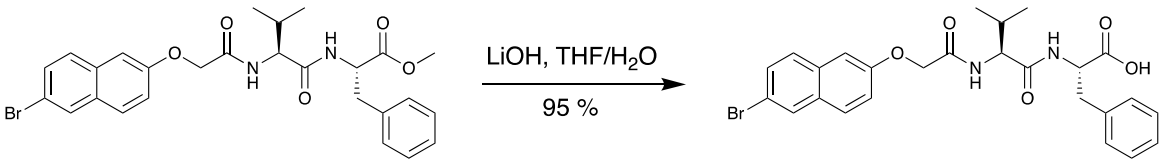
Scheme S10. Synthesis of 6Br2NapVOH
To a solution of 6Br2NapVOMe (7.30 g, 18.5 mmol) in tetrahydrofuran (100 mL) was added a solution of lithium hydroxide (5 eq, 2.20 g) in water (100 mL) and the reaction was monitored by TLC. After about one hour, the starting material had been consumed. The mixture was poured into 1M hydrochloric acid (ca. 500 mL) and stirred for one hour. The precipitated sticky solids were filtered off and washed with water in the filter. Recrystallization from boiling acetonitrile afforded the compound 6Br2NapVOH as a white solid (6.85 g, 97 %).

δH(400 MHz, DMSOd6): 8.39 (1H, d, *J* 8.4 Hz, N**H**), 7.45 (1H, d, *J* 8.6 Hz, N**H**), 8.26-7.31 (6H, m, **Aro**), 4.82 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$), 4.79 (1H, d, *J* 14.4 Hz, C$\mathbf{H}_2$), 4.32 (1H, dd, *J* 8.5, 6.7 Hz, *C**H**), 2.09 (1H, m, C**H**$(CH_3)_2$), 0.84 (6H, dd, *J* 6.8, 5.1 Hz, CH(C$\mathbf{H}_3)_2$). **δC (100 MHz, DMSO-d6):** (100 MHz, DMSO-d_6) 171.0, 169.7 (C=O), 156.3, 132.8, 129.6, 129.4, 129.2, 129.0, 128.3, 119.8, 116.5, 107.0 (CAr), 66.6 (CH_2), 56.2 (*CH), 28.9 (**C**H$(CH_3)_2$), 19.0, 18.3 CH(**C**$H_3)_2$).



Scheme S11. Synthesis of 2NapVFOMe

To a suspension of 6Br2NapVOH (6.85 g, 18 mmol) in chloroform (80 mL) was added isobutyl chloroformate (1 eq, 2.33 mL) followed by *N*-methylmorpholine (1 eq, 1.98 mL). After 10 minutes, L-phenylalanine methyl ester hydrochloride (1.0 eq, 3.88 g) and another portion of *N*-methylmorpholine (1 eq, 1.98 mL g) were added and the reaction was stirred overnight. After this time, it was diluted with an approximately equal amount of chloroform, washed in turn with water (2×), 1M hydrochloric acid and brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The resulting white solid of 6Br2NapVFOMe (8.14 g, 86 % crude) was used as is in the next step.
δH(400 MHz, DMSOd6): 8.54 (1H, d, *J* 7.4 Hz, N**H**), 7.9 (1H, d, *J* 9.1 Hz, N**H**), 8.14-7.14 (11H, m, **Aro**), 4.71 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$), 4.66 (1H, d, *J* 14.4 Hz, C$\mathbf{H}_2$), 4.48 (1H, m,*C**H**), 4.29 (1H, dd, *J* 9.0, 6.5 Hz, *C**H**), 3.56 (3H, s, OC$\mathbf{H}_3$), 3.02 (1H, dd, *J* 14.0, 6.1 Hz, C$\mathbf{H}_2$-Phe), 2.91 (1H, dd, J 13.9, 8.8 Hz, C$\mathbf{H}_2$-Phe), 1.99 (1H, m, C**H**-CH_2-Phe), 0.80 (6H, dd, *J* 6.8, 19.8 Hz, CH(C$\mathbf{H}_3)_2$). **δC (100 MHz, DMSO-d6):** (100 MHz, DMSO-d_6) 172.7, 170.5, 167.3 (C=O), 155.9, 135.5, 132.6, 129.7, 129.6, 129.4, 129.0, 128.6, 128.5, 127.9, 126.4, 119.6, 116.5, 107.3 (C_{Ar}), 66.8 (CH_2), 56.9, 53.5 (*CH), 50.4 (OCH_3), 36.5 (**C**H-$(CH_3)_2$, 30.9 (**C**H_2-Phe), 19.1, 17.1 (CH-(**C**$H_3)_2$).



Scheme S12. Synthesis of 6Br2NapVFOH
To a solution of 6Br2NapVFOMe (8.14 g, 15 mmol) in tetrahydrofuran (100 mL) was added a solution of lithium hydroxide (5 eq, 1.80 g) in water (100 mL) and the reaction was monitored by TLC. After about one hour, the starting material had been consumed. The mixture was poured into 1M hydrochloric acid (ca. 500 mL) and stirred for one hour. The precipitate was filtered off, then washed with several portions of water. Drying by azeotropic distillation with acetonitrile on a rotary evaporator, followed by keeping at 40 °C under vacuum overnight, affording the compound 6Br2NapVFOH (7.50 g, 95 %).
δH(400 MHz, DMSOd6): 12.71 (1H, s, O**H**), 8.37 (1H, d, *J* 7.8 Hz, N**H**), 8.12 (1H, d, *J* 1.9 Hz, N**H**), 7.92-7.12 (11H, m, **Aro**), 4.71 (1H, d, *J* 14.7 Hz, C$\mathbf{H}_2$), 4.66 (1H, d, *J* 14.6 Hz, C$\mathbf{H}_2$), 4.43 (1H, m, *C**H**), 4.29 (1H, dd, *J* 9.0 , 6.5 Hz, *C**H**), 3.04 (1H, dd, *J* 13.9, 5.2 Hz, CH-C$\mathbf{H}_2$-Phe), 2.88 (1H, dd, *J* 13.9, 9.1 Hz, CH-C$\mathbf{H}_2$-Phe), 1.99 (1H, m, C**H**-CH_2-Phe), 0.79 (6H, dd, *J* 21.5, 6.7 Hz, CH-(C$\mathbf{H}_3)_2$). **δC (100 MHz, DMSO-d6):** 172.7, 170.6, 167.1 (C=O), 155.9, 137.5, 132.6, 129.9, 129.4, 129.4, 129.0, 128.8, 128.7, 128.1, 126.4, 119.6, 116.6, 107.4 (C_{Ar}), 66.8 (CH_2), 56.9, 53.4 (*CH), 36.6 (**C**H-$(CH_3)_2$, 30.9 (**C**H_2-Phe), 19.1, 17.7 (CH-(**C**$H_3)_2$). **HRMS (ESI) m/z:** $[M+Na]^+$ accurate mass calculated for $C_{26}H_{27}N_2NaO_5{}^{79}Br$: 549.1001, Found: 549.0988.

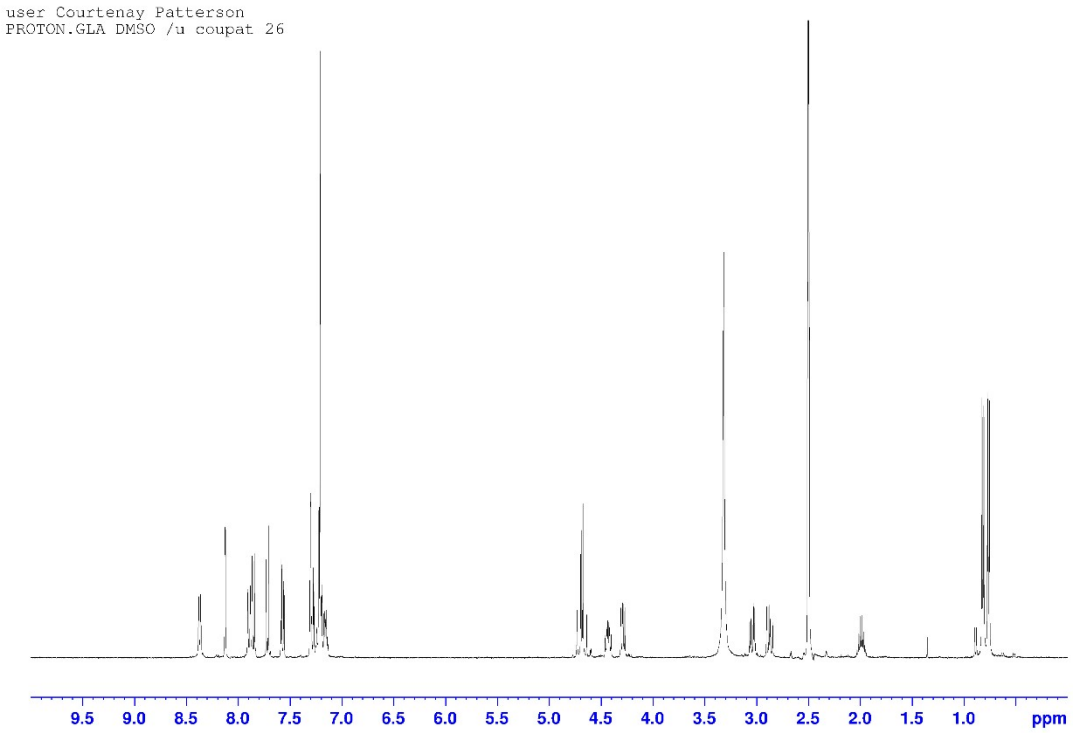


Figure S2. Proton NMR spectrum of 6Br2NapVFOH in d_6-DMSO.

2 Preparation of stock solutions

Each stock solution was prepared to a volume of 200 mL. The appropriate mass of gelator was weighed out in a 250 mL glass jar. 1 molar equivalent of NaOH (aq. 0.1 M) was added and then the stock solution made up to a volume of 200 mL using deionized water. Solutions were left to stir overnight to ensure all gelator had dissolved and the desired concentration was reached. Solutions were then adjusted to pH 8 using HCl (aq. 1 M) and NaOH (aq. 1 M) as necessary. All stock solutions were stored at room temperature and made fresh at the beginning of every week.

3 Image analysis

Images of the gel-forming on the electrode surface were taken every 30 seconds using a Panasonic Lumix DMC-FZ200 camera and custom-built programmable shutter release timer. These images were uploaded to the open-source image analysis software 'ImageJ'. The outline of the gel in each image was then traced, allowing the volume of the gel to be calculated (Figure S3). Once the area of all the images were calculated the rate of gel growth could then be plotted (Figure S4).

4 pH measurements

A FC200 pH probe from HANNA instruments with a 6 mm x 10 mm conical tip was used for pH measurements. The stated accuracy of the pH measurements is ±1. The tip was placed in the stock solution and the pH was adjusted using HCl (aq. 1 M) and NaOH (aq. 1M). After the addition of each aliquot of HCl/NaOH, the solution was stirred for 30 seconds. The stirring was stopped, and another measurement was taken. This process was repeated until the desired pH of 8 was reached.

5 Electrochemical measurements

The electrochemical set up shown in Figure S5. was used to carry out cyclic voltammetry and grow gels using fast chronopotentiometry. All experiments were run using a Dropsens potentiostat. Cyclic voltammetry measurements were carried out within a potential range of -0.5 to 1.2 V vs. an Ag/AgCl

(3 M) ref. at a scan rate of 0.2 V/s (Figure S6). This was used to determine the current value to grow gels using fast chronopotentiometry. Each CV measurement consisted of one scan. An appropriate current value was then chosen from the middle of the oxidation curve, this current was then imposed on the gelator/HQ/electrolyte solution for the chosen time using fast chronopotentiometry (Figure S7). Once the experiment was finished the gel was removed using a spatula.

6 Gel forming procedure on 12 mm electrode under nitrogen

Stock solutions were prepared as described in Section 2. 200 mL of gelator solution was then transferred to a double-necked round bottom flask and degassed by stirring under vacuum for 30 minutes in a fume hood (Figure S8a). After this time, the stirring was stopped. The nitrogen inlet on the other neck of the flask was then turned on and the vacuum was continued for 3-5 seconds before turning both the vacuum and the nitrogen off. The stopper was then removed and 1 g of hydroquinone and 2 mL of NaCl (0.1 M) were quickly added and the stopper replaced. The solution was then stirred under vacuum for a further 10 minutes to ensure all hydroquinone had dissolved. While the solution was degassing, the three-electrode system (12 mm glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl (3 M) reference electrode) was set up in a 250 mL bowl within a desiccator (Figure S8c). The desiccator lid was replaced and the rim secured with a layer of parafilm to prevent air leaks. A custom-made 3D printed lid with three holes (one for nitrogen inlet, one for electrode wires and one for working electrode) was placed on top of the desiccator neck and secured using sellotape (Figure S8b). A nitrogen inlet was placed inside the desiccator and a steady flow of nitrogen was applied for 30 minutes to degass the desiccator chamber. After the hydroquinone had dissolved the stirring was stopped and the vacuum switched off. The stopper was then replaced with a Drechsel bottle head. One of the two bottle heads necks was attached to the nitrogen inlet and the other attached to a tube that feeds through the desiccator lid and into the bowl within the desiccator (Figure S8d). The nitrogen inlet tube for the desiccator chamber was turned off and removed to allow the Drechsel bottle tube to be inserted. The degassed solution was then transferred by turning on the nitrogen inlet, pushing the solution through the tube and into the bowl. Once the solution had been transferred, the tube is removed and replaced with the nitrogen inlet tube, again applying a steady flow of nitrogen for the remainder of the experiment. The gels were then grown electrochemically as described in Section 5. Once the gels were grown, they were removed from the solution and carefully slid off the electrode using a spatula (Figure S9).

6.1 Multilayered gel forming procedure on 12 mm electrode.

The first layer of the multilayered gel was grown as described in Section 6 (Figure S10a). After the gel forming procedure was complete, the lid of the desiccator was lifted and the electrode with gel attached was carefully placed to one side. The remaining gelator solution in the bowl was drained and the bowl rinsed thoroughly. The bowl was then placed back in the desiccator, followed by fixing the desiccator lid and electrode with gel attached back in position. The second degassed gelator solution was then immediately added to the desiccator bowl as described in Section 6. The gel fabrication process was then repeated. Once the deposition process was complete the gel was removed from the solution and detached from the electrode using a spatula (Figure S10c).

7 Cavitation Rheology

The cavitation rheometer was custom-made and the experimental procedures used here are as described previously (Figure S11).[2] Measurements were run using a 60 mL syringe (HSW HENKE-JECT Syringe Syringe with Luer-lock attachment) with an inner diameter of 0.41 mm (Fisher Scientific, HamiltonTM Kel-F Hub Blunt Point Needle with Luer-lock attachment). A 4.0 mL min^{-1} pump rate was used throughout.

7.1 Cavitation Rheology for multi-layered gels.

Cavitation rheology measurements were taken as previously described in Section 7. However, in order to collect measurements from the multi-layered gel, the layers must be exposed. Using a scalpel, a 1 cm cross section from the multi-layered gel was cut as shown in Figure 12. The cross section of the sample was then used to collect the measurements. To take measurements from each layer, the needle was moved and lowered into the target layer.

8 Determining relative gelator concentration using ^{1}H NMR spectroscopy

^{1}H NMR spectra were recorded using a Bruker Avance III 500 MHz spectrometer. Samples were run in DMSO-d_6. To determine the gelator concentration within the gels, ^{1}H NMR spectra were collected of the freeze-dried gels. Once gel deposition was complete the gels were removed from the electrode and placed in a freezer for two hours. For the multi-layered gels, the gel was first removed from the electrode before cutting a 1 cm cross section (Figure S11b). The layers were then separated at the boundary of the two gels using a scalpel. Each layer was then frozen. The frozen gels/gel layers were then transferred to the freeze dryer (CHRIST, Alpha 2-4 LSCbasic) and left overnight. The freeze-dried gels were then dissolved in 1 mL of DMSO-d_6 and pipetted into an NMR tube containing a lock tube of known concentration (1% PDMS in C_2Cl_4). This was used as the external standard. The gelator concentration within the gels was then calculated using quantitative NMR (qNMR).

9 Powder X-Ray Diffraction (PXRD)

PXRD (powder X-ray diffraction) patterns were collected using a Rigaku MiniFlex 6G equipped with a D/teX Ultra detector, a 6-position (ASC-6) sample changer and Cu sealed tube (Kα1 and Kα2 wavelengths - 1.5406 and 1.5444 Å respectively). Patterns were measured as $\theta/2\theta$ scans typically. Data collection and analysis were carried out using Rigaku SmartLab Studio II software (Rigaku Corporation, 2014).

Supplementary Figures

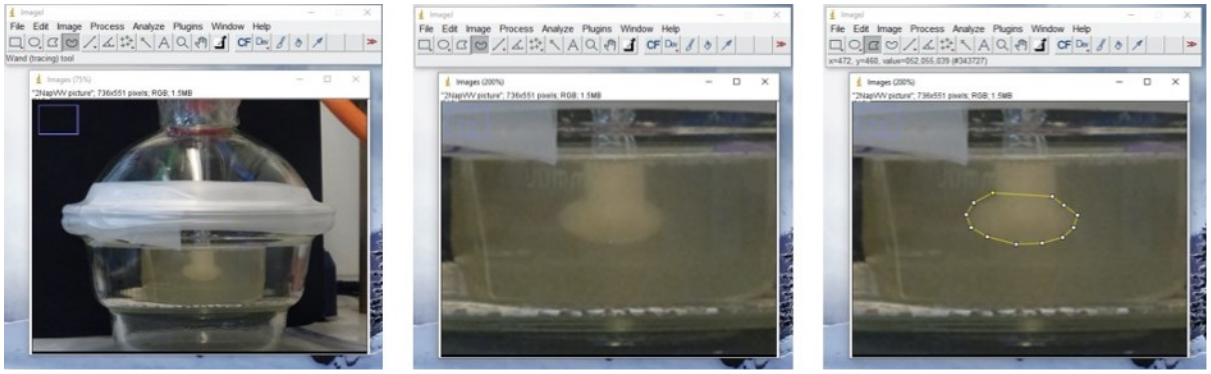


Figure S3. ImageJ software is used to trace around the gel to determine the change in gel cross sectional area with time.

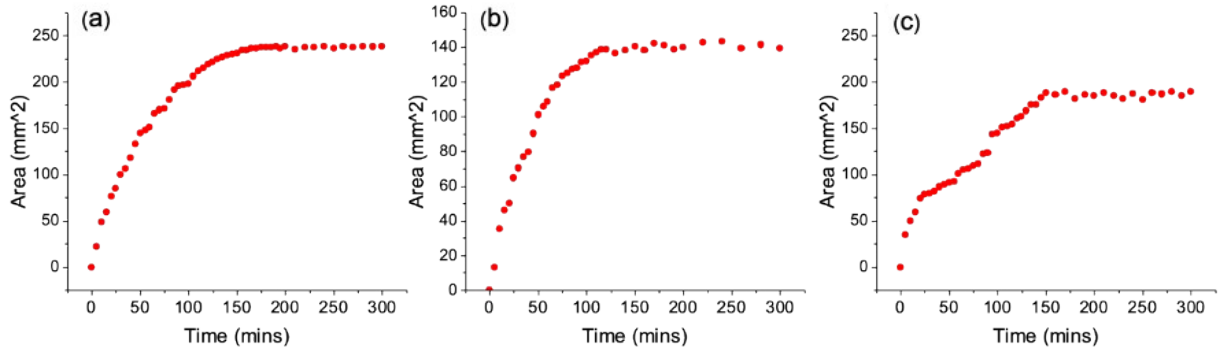


Figure S4. Rate of gel growth with time (a) 2NapVVV (b) 6Br2NapAV (c) 2NapAA.

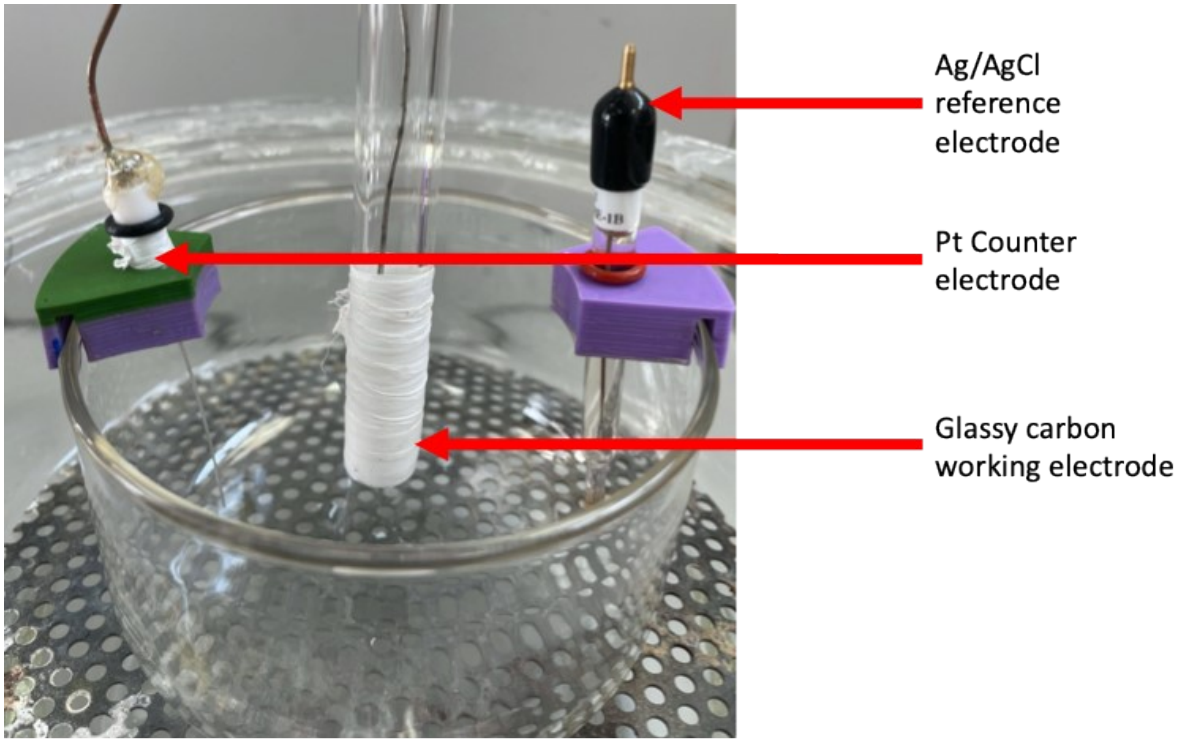


Figure S5. Electrochemical set up within desiccator chamber.

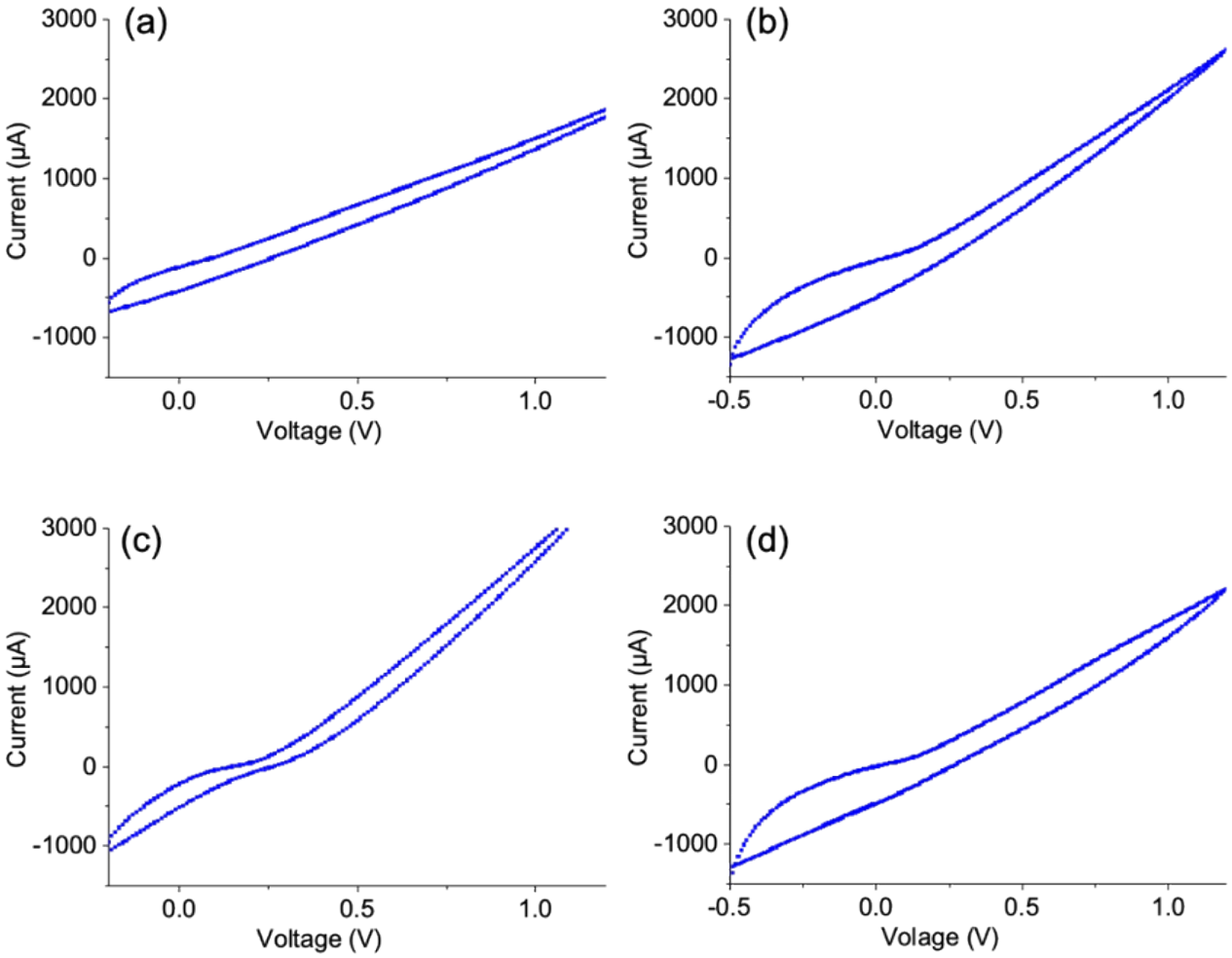


Figure S6. Cyclic Voltammograms of (a) 2NapVVV (b) 6Br2NapVF (c) 2NapAA (d) 6Br2NapAV. Initial conditions [gelator] = 5 mg/mL, [HQ] = 5 mg/mL, [NaCl] = 0.1 M, [pH] = 8.

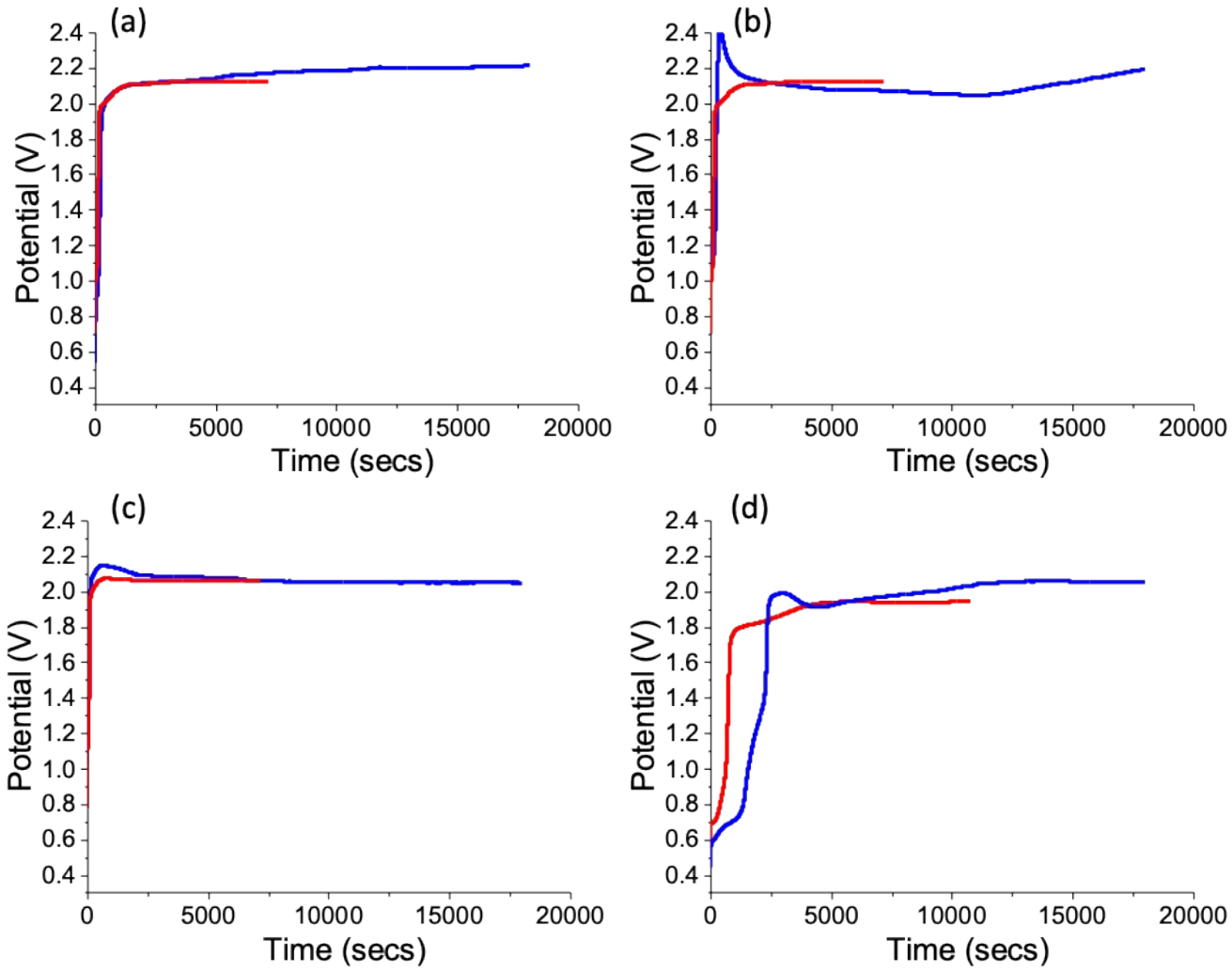


Figure S7. Potential vs time transients for (a) 2NapVVV (b) 6Br2NapVF (c) 2NapAA (d) 6Br2NapAV.

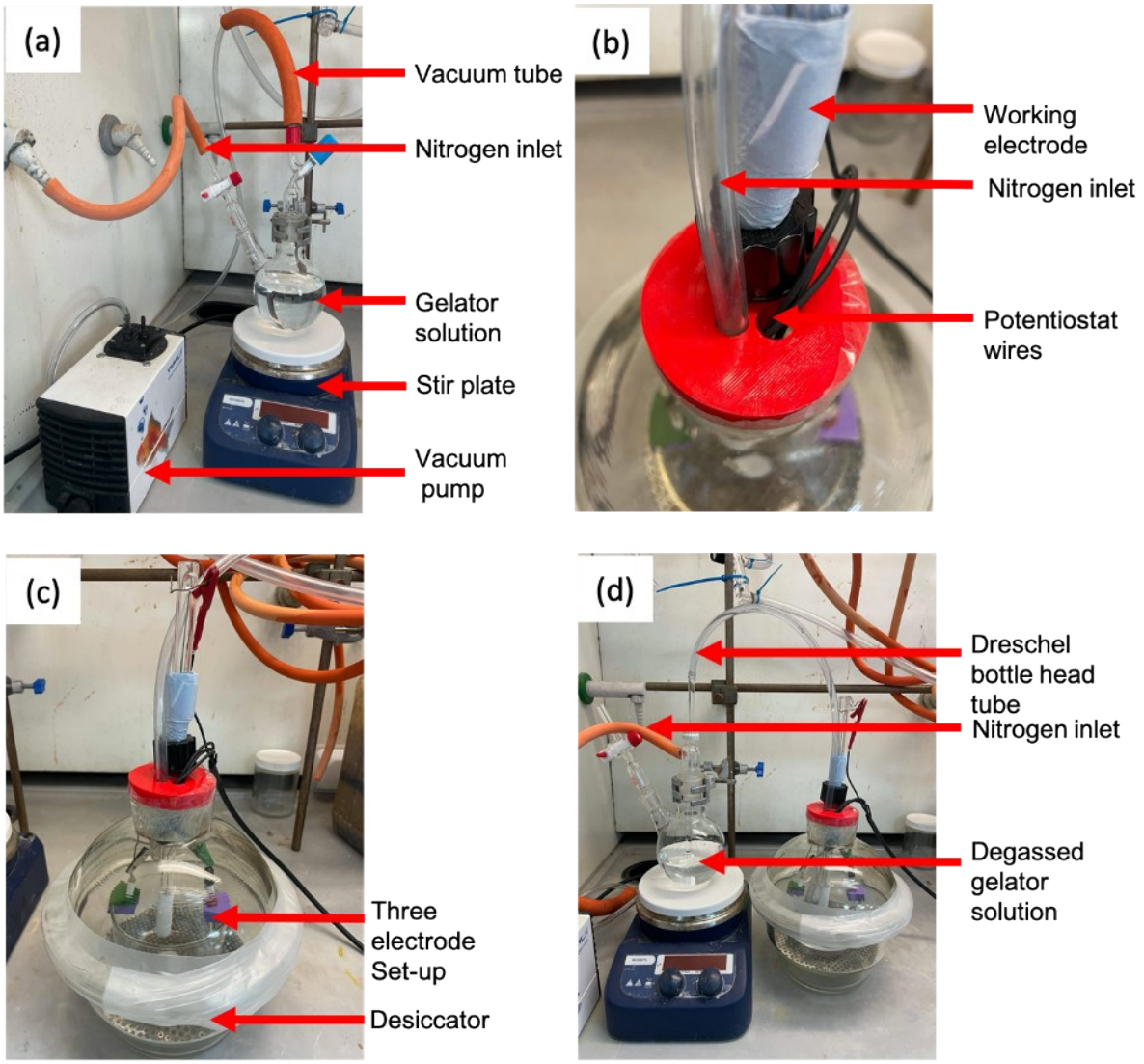


Figure S8. Set up for growing dipeptide gels under nitrogen via the electrochemical oxidation of hydroquinone. (a) degassing of gelator/HQ solution (b) custom made 3D printed desiccator lid (c) Electrochemical set up within desiccator chamber (d) Set up used to transfer degassed gelator/HQ solution into desiccator chamber.

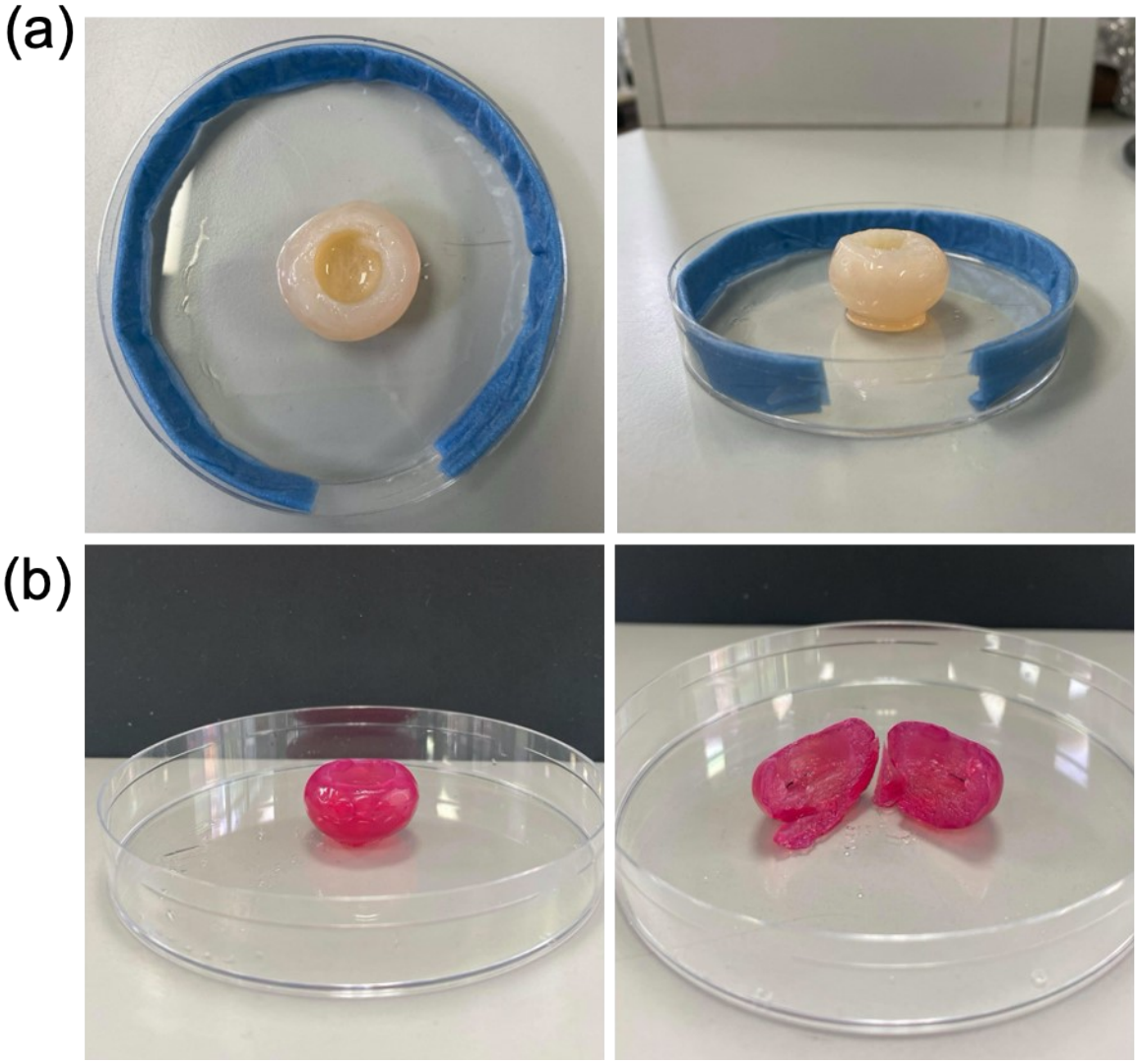


Figure S9. (a) 6Br2NapVF gels grown via HQ oxidation (b) 6Br2NapVF gels grown via HQ oxidation in the presence of universal indicator. Gel was cut to show homogenous pH throughout the sample. Initial conditions in both cases: [pH] = 8, [gelator] = 5 mg/mL, [HQ] = 5 mg/mL, [NaCl] = 0.1 M

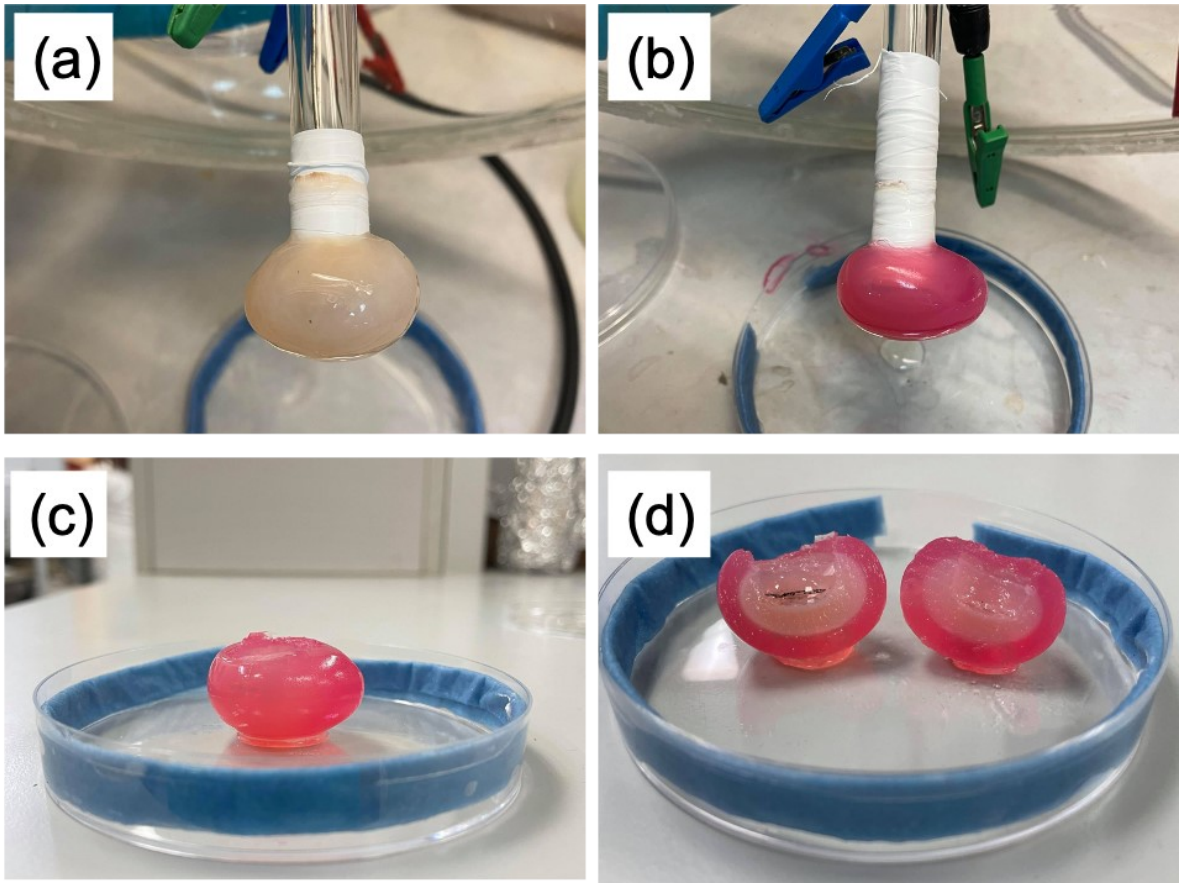


Figure S10. Formation of multi-layered gel (a) 6Br2NapVF inner layer (b) 2NapVVV outer layer. Universal indicator added to 2NapVVV solution to help visualise the layers. (c) multi-layered gel of 6Br2NapVF and 2NapVVV detached from electrode (d) Cross section of multi-layered gel.

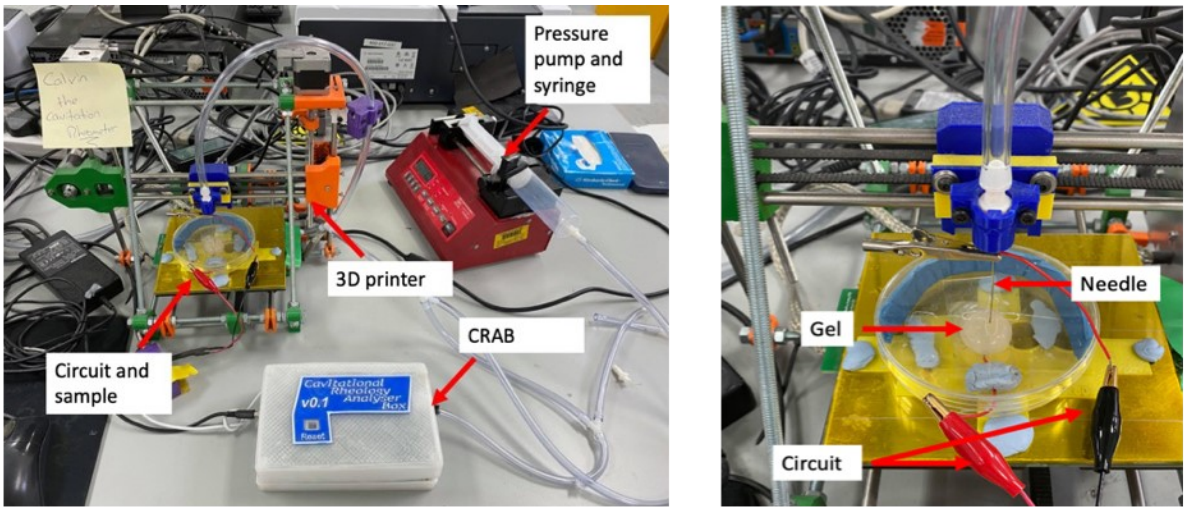


Figure S11. Cavitation rheometer set up.

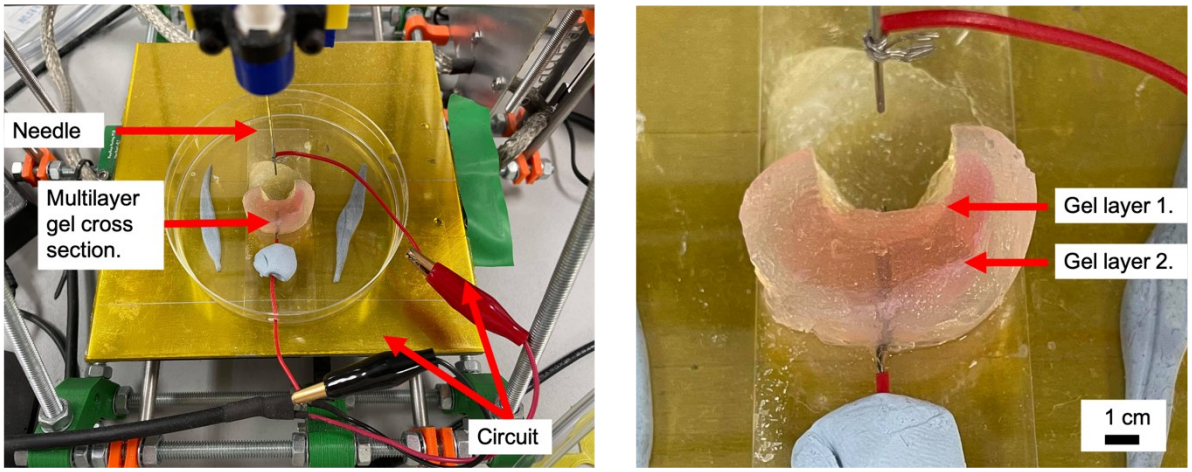


Figure S12. (a) Cavitation rheometer set up for multi-layered gels (b) A cross section from the multi-layered is used when collecting the measurements.

References

1. L. Chen, S. Revel, K. Morris, L. C. Serpell and D. J. Adams, *Langmuir*, 2010, **26**, 13466-13471.
2. A. M. Fuentes-Caparrós, B. Dietrich, L. Thomson, C. Chauveau and D. J. Adams, *Soft Matter.*, 2019, **15**, 6340-6347.