Supplementary Material (ESI) for Chemical Communications

Low Molecular Weight Gelator – Dextran Composites

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SUPPORTING INFORMATION

Experimental

Materials: All chemicals and solvents were purchased from Sigma-Aldrich and used as received.

Dipeptide-conjugate Synthesis: The dipeptide-conjugates were prepared as described previously.

Gel Formation: Different quanities of dextran were added into 2 mL deionised water to prepare the dextran-water solutions at different concentrations. Homegenous and transparent solutions were obtained after stirring overnight strring The dipeptide derivative (10.0 mg) was suspended in the dextran-water (2.00 mL) solution. The final concentration of dipetide is 0.5 wt%. An equimolar quantity of NaOH (0.1 M, aq), around 0.26 mL, was added and the solution gently stirred for 30 minutes until a clear solution was formed. The pH of this solution was measured to be 10.3. To prepare hydrogels, solutions were added to measured quantities of glucono-δ-lactone (GdL) (8.7 mg/ml) and the samples left to stand for 24 hours or, for the rheology measurements, transferred directly onto the plate.

Rheology: Dynamic rheological experiments and viscosity measurements were performed on an Anton Paar Physica MCR101 rheometer. For the oscillatory shear measurements, a

sandblasted parallel top plate with a 50 mm diameter and 0.9 mm gap distance were used. Gels for rheological experiments were prepared on the bottom plate of the rheometer by loading a 2.0 mL solution of the gelator immediately after GdL addition. At this point, the sample is still a free-flowing liquid. Hence, sample uniformity and reproducibility is high. Evaporation of water from the hydrogel was minimized by covering the sides of the plate with low viscosity mineral oil. The measurements of the shear modulus (storage modulus G' and loss modulus G'') with gelation were made as a function of time at a frequency of 1.59 Hz (10 rad/s) and at a constant strain of 1 % for a period of 24 hours. For the viscosity measurements and the rotation tests, standard cone-plate geometry (CP75 with the diameter 75mm and angle 1^{o}) were used. The viscosity of dextran-water solutions was measured in the shear rate range between 0.1 and 100 s^{-1}. The viscosity of all solutions is independent on the shear rate because the property of ideal-viscous liquid of dextran-water solutions.

Confocal Microscopy: Confocal microscopy images were taken using a Zeiss LSM710 microscope using a 100X 1.45 NA alpha plan-fluar objective using a pinhole diameter of 1 airy unit. Fluorescence from Nile blue was excited using a 633nm helium neon laser and emission was detected above 650nm.

Transmission Electron microscopy: Samples for examination by TEM were prepared on formvar/carbon film coated 400-mesh copper grids (Agar scientific). The required amount of GdL was added to a solution of dipeptide derivative (0.5wt% solution at pH 10.7) and allowed to gelate. The gel was sampled by placing on a grid and allowing adsorption for 1 minute followed by a 1 minute wash and two 1 minute negative stains using 2 % w/v uranyl acetate. Negatively stained grids were allowed to dry and examined on a Hitachi-7100 TEM operated at 100 kV. Images were acquired digitally using an axially mounted (2000 × 2000 pixels) Gatan Ultrascan 1000 CCD camera (Gatan, Oxford, UK).

Dextran M_r / mg.ml^{-1}	η (mPa· s) (dextran concentration = 17 wt%)	η (mPa· s) (dextran concentration = 0.5 wt%)
2,000,000	240	3.3
100,000	43.4	3.1
40,000	34	3.0
6,000	7.4	2.9

Table S1. Viscosity of solutions of dextran of different molecular weight at different concentrations. The data is reported for solutions at pH 6.5; at higher pH, no noticeable difference was observed.

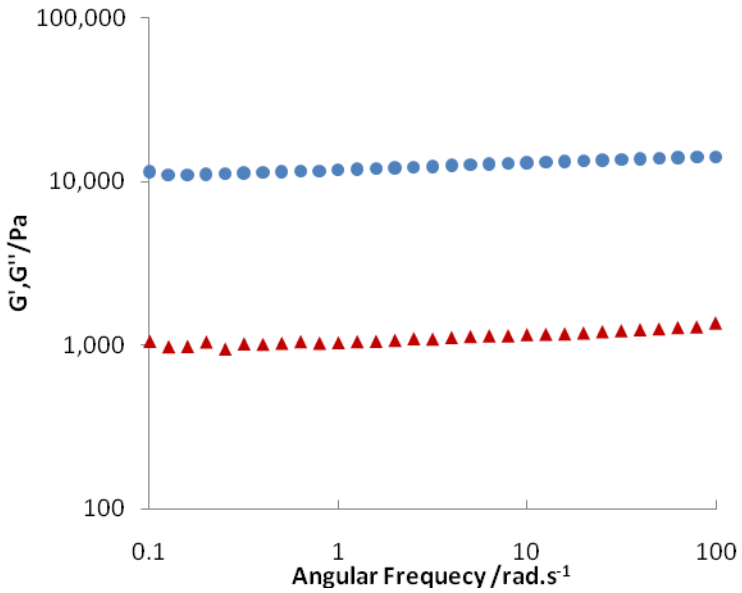

Figure S1. The dependence of storage modulus (G', blue circles) and loss modulus (G'', red triangles) with angular frequency for dipeptide-dextran (2,000,000 g/mol, 5wt%) gel after gelation under the strain of 1%.

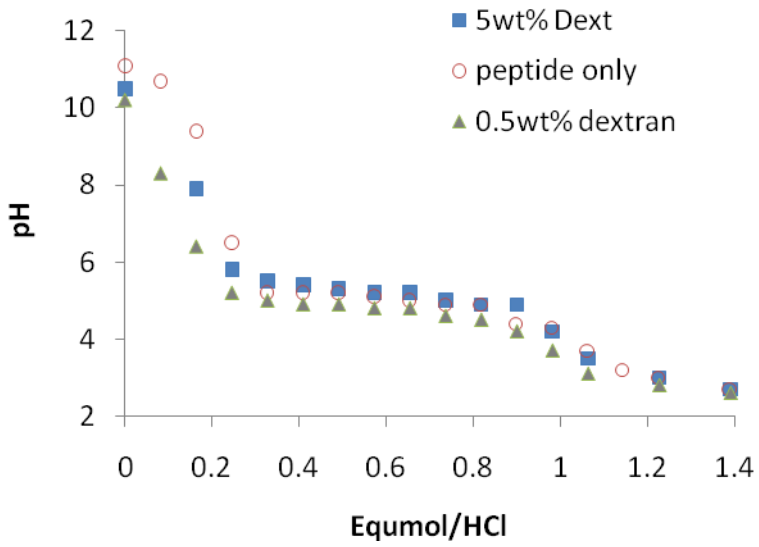

Figure S2. Titration data for dipepitde-conugate **1** (0.5 wt%) alone and in the presence of different concentrations of dextran (2,000,000 g/mol) with HCl (aq, 0.1M). Data for titrations in the presence of higher concentrations of dextran could not be obtained due to the high viscosity of the solutions resulting in highly inhomogeneous mixing.

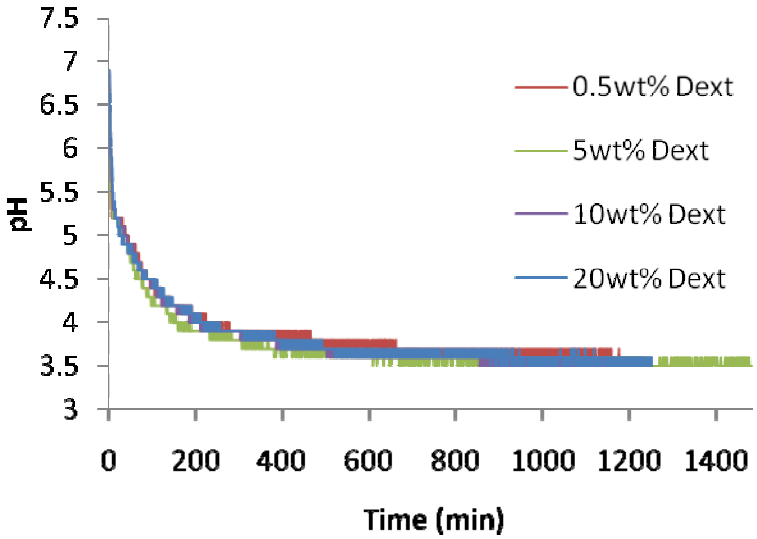

Figure S3. Plot of pH against time for solutions of dipeptide-conjugate **1** in the presence of different concentrations of dextran (2,000,000 g/mol) on addition of GdL (8.7 mg/mL) from a starting pH of 10.3.

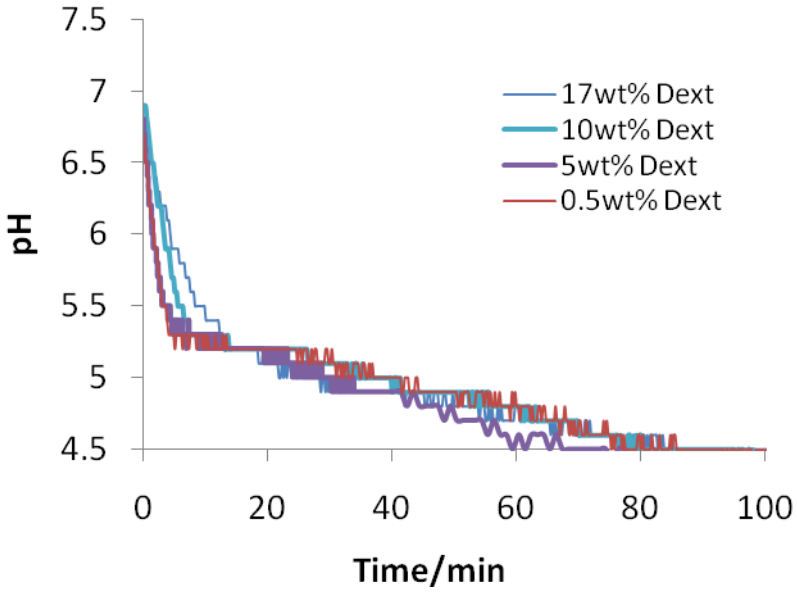

Figure S4. Expansion of Figure S3 showing the plot of pH against time for the first 100 minutes for solutions of dipeptide-conjugate **1** in the presence of different concentrations of dextran (2,000,000 g/mol) on addition of GdL (8.7 mg/mL) from a starting pH of 10.3. The rate of pH change differs at early times for different concentrations of dextran.

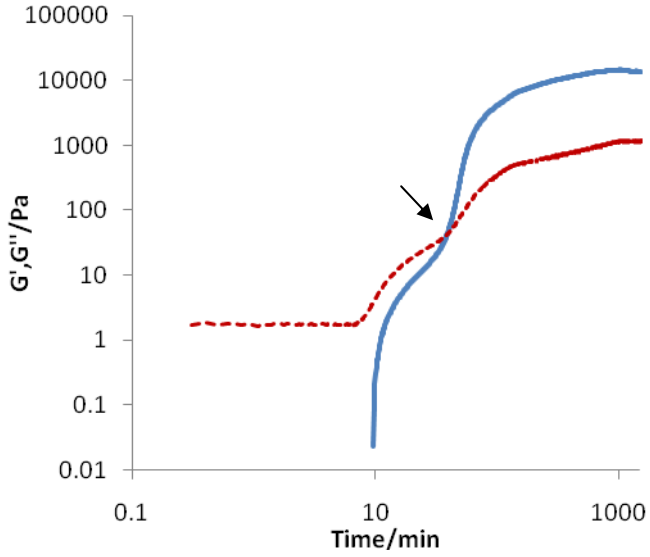

Figure S5. Evolution curves of storage modulus (G', blue solid line) and loss modulus(G'', red dot line) during the gelation process of dipeptide solution with 17wt% dextran (Mr=2,000,000 g/mol) .

To see the early stage clearly, the scales of axis were plotted on a logarithmic scale. The gelation time was determined by the cross-over point as shown as arrow in the figure.

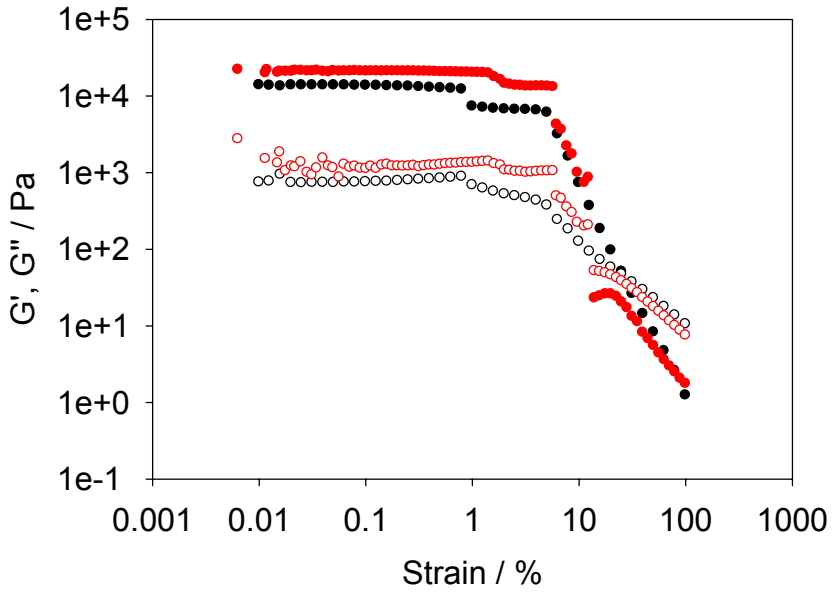

Figure S6. Amplitude sweep for hydrogels with 0% dextran (red data) and 17 wt% dextran (black data).

	G' / Pa	**G'' / Pa**	**Gelation time / min**
Dipeptide alone	18375	1289	16
Dipeptide + PEO	3509	574	34
Dipeptide + dextran	11539	1303	60

Table S2. Comparison of the storage modulus (G') and loss modulus (G'') achieved after 24 hours from the gelation process with no added polymer, PEO (3wt% , Mr=400,000 g/mol, η = 317 mPa/s) or dextran (17 wt%, Mr=2000,000 g/mol, η = 240 mPa/s). Data were obtained under strain of 1% and frequency of 10 rad/s.