

## Supplementary materials for Gels and Threads: Mussel-inspired One-pot Route to Advanced Responsive Materials

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### EXPERIMENTAL SECTION:

#### Hydrogel formation

The hydrogels were formed by dissolving 2.2 mg TA (Sigma Aldrich, CAS no. 1401-55-4) and 19.9 mg PAA (120-200 kMW, Polysciences Inc., CAS no. 71550-12-4) in 75  $\mu\text{L}$  demineralized  $\text{H}_2\text{O}$ , resulting in a pH 1.5 solution. The resulting solution was mixed with 1/6 final volume (25  $\mu\text{L}$ ) 0.0865 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution (Sigma Aldrich, CAS no. 10025-77-1) to establish the TA: $\text{Fe}^{\text{III}}$  cross-links at low pH (pyrogallol to  $\text{Fe}^{\text{III}}$  molar ratio of 3:1). A very dark green/blue color developed instantly upon mixing (Figure 1a). The hydrogel network was established by adding 2/6 final volume NaOH (50  $\mu\text{L}$ ) with a concentration adjusted to obtain the requested final pH of the hydrogel. Where the droplet made contact with the polymer solution, the color immediately changed to a dark red color (Figure 1a) due to the formation of tris-species. Homogeneous hydrogels were obtained after mixing the components for approximately one minute (Final TA and PAA concentration: 14.7 mg/mL and 133 mg/mL, respectively).  $\text{Al}^{\text{III}}$  based hydrogels were formed using the same approach but with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  as the metal source (Figure S1a). Polylysine (PL)/TA/ $\text{Fe}^{\text{III}}$  hydrogels were formed following the same overall procedure; however, with 44 mg poly-L-lysine hydrobromide (Sigma Aldrich, CAS no. [25988-63-0](#)) instead of PAA (Figure S1b).

The pH of the hydrogels was measured using a flat surface Fieldcount Soilstick electrode (Spectrum Technologies, Plainfield, Illinois). Prior to experiments, the hydrogels were allowed to rest for 1 h to facilitate relaxation of the polymer network.

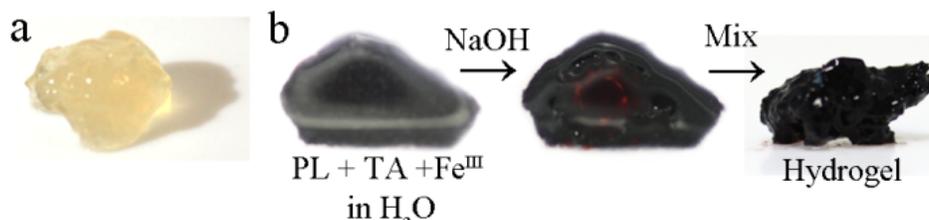


Figure S1: a) TA/PAA/ $\text{Al}^{\text{III}}$  based hydrogel (pH 6). B) Pictures illustrating the different steps involved in the hydrogel formation of Polylysine (PL)/TA/ $\text{Fe}^{\text{III}}$  hydrogels.

#### Thread formation

Threads were spun from mixtures of  $\text{M}^{\text{III}}$ /TA/PAA with a concentration 15 times higher than the original hydrogel recipe (220 mg/ml TA, 1990 mg/ml PAA, pyrogallol to  $\text{M}^{\text{III}}$  molar ratio of 3:1,  $\text{M}^{\text{III}}$ :  $\text{Fe}^{\text{III}}$ / $\text{Al}^{\text{III}}$ ). PAA and TA were dissolved in 0.1 M HCl to insure a low pH of the solution. The thread diameter was determined using an Olympus bx51 microscope (Figure S2).

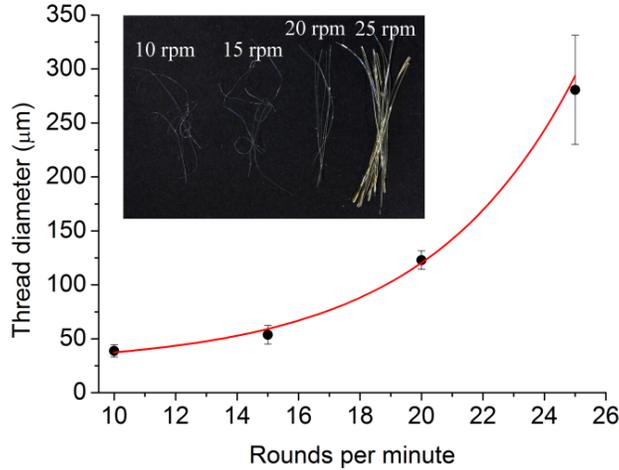


Figure S2. Thread diameter (Al<sup>III</sup>/TA/PAA) plotted as a function of the number of rounds per minute ( $n = 10$ ). The red line serves as a guide to the eye. The insert shows a picture of the threads.

Video V1 and 2. See text for details

The sensitivity of the threads towards humidity was investigated. Threads were formed at 30 % humidity (20°C) and exposed to 45 % humidity while monitoring their weight gain on a high precision scale (Cubis MSU125P-100-DI). Figure

$$m_{gain} = \frac{m - m_{start}}{m_{start}}$$

S3a depicts the relative mass gain ( $m_{gain} = \frac{m - m_{start}}{m_{start}}$ ) for three different samples plotted as a function of time. All curves follow a Boltzmann function, meaning that absorption of water is high at the beginning and levels off, reaching a plateau after ~20 minutes. The data shows that the final mass gain  $m_{gain}(60 \text{ min})$  depends on the initial mass of the thread. The higher the initial mass, the lower relative mass gain (Figure S3b). This correlation can be explained by means of the surface-area-to-volume ratio. A sample with a large mass has a larger size and consequently, a lower surface-area-to-volume ratio than a sample with a low mass. Accordingly, it adsorbs less water per mass, resulting in a lower final relative mass gain.

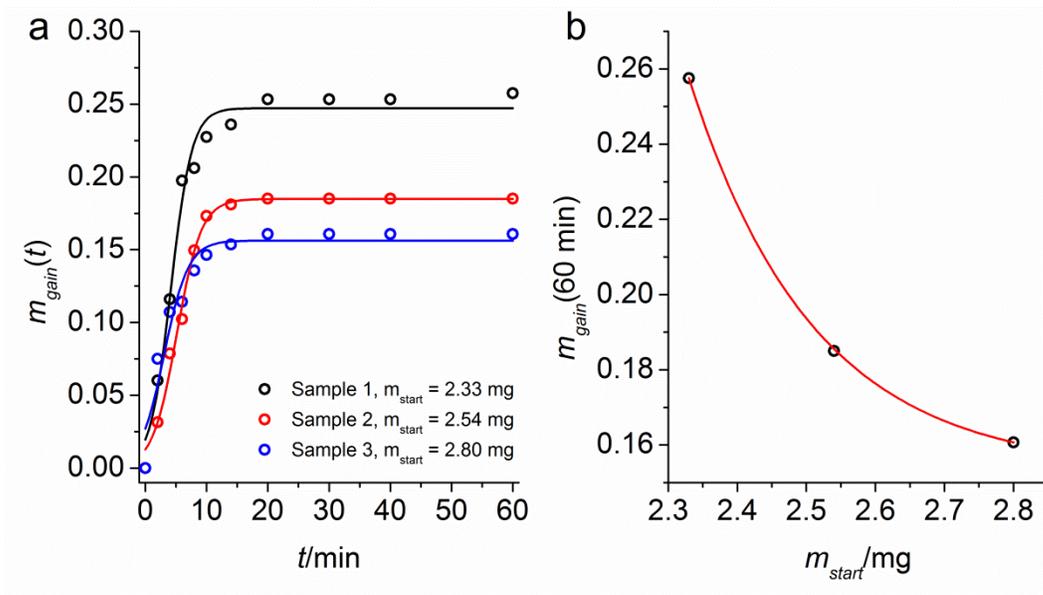


Figure S3. a) The relative mass gain at 45% humidity (20°C) plotted as a function of time for three different samples with different starting mass ( $m_{start}$  of 2.33 mg, 2.54 mg and 2.80 mg). The black, red and blue lines show the fitted

Boltzmann curves. b) The final mass gain  $m_{gain}$  (60 min) plotted as a function of the initial mass of the threads. The red line serves as a guide to the eye.

The tensile strength was estimated by loading a single thread (3 cm long, diameter  $\sim 225 \mu\text{m}$ ) suspended from a glass wire (Figure S4). Prior to loading, the threads were dried in a stream of nitrogen for 5 minutes ( $20^\circ\text{C}$ ) and exposed to one of the following conditions: 1) 2 minutes rest at 40% humidity ( $20^\circ\text{C}$ , dry conditions), 2)  $\text{NH}_3$  gas for 2 minutes or 3) after one of the aforementioned conditions followed by 2 minutes at 90% humidity ( $25^\circ\text{C}$ ). The load on the thread was increased by slowly adding water to the attached beaker (Figure S4). The yield weights were converted into tensile strengths (TS) by means of the following equation:

$$TS = \frac{F_{gravity}}{A_{thread}} = \frac{m_{load} \cdot g}{A_{thread}}$$

where  $F_{gravity}$  is the gravitational force,  $A_{thread}$  is the cross-sectional area of the threads,  $m_{load}$  is the mass of the applied load and  $g$  is the gravity.



Figure S4. a) Schematic of the experimental setup used to test the tensile strength of the individual fibers under various conditions.

#### UV/VIS absorption

6 mL stock solution of  $\text{Fe}^{\text{III}}$ , TA and PAA in 0.1 M HCl was prepared with a  $\text{Fe}^{\text{III}}$  to pyrogallol ratio of 1:3 ( $\sim$  factor 2.5 lower than the original hydrogel recipe, TA and PAA concentration of 5.9 mg/mL and 53 mg/mL, respectively). The pH was gradually increased by titration with NaOH, whilst the pH was monitored with a Metrohm pH meter equipped with a Metrohm unitrode. The pH was increased in steps of one pH units from pH 1 to a final pH of 12 and the spectral changes were monitored by performing UV-VIS absorption measurement at every step using a UV-Visible absorption spectrophotometer (PerkinElmer Lambda 25) equipped with quartz cuvettes (path length: 1 cm). The absorption profiles were collected from 300-1,000 nm at ambient temperature (Figure S5).

The relative abundances of the mono-, bis- and tris- complexes were deduced by fitting a multi-Gauss function in an iterative manner to the collected absorption profiles. Consequently, models for the characteristic bands associated with the mono-, bis- and tris-complex were proposed that could describe all absorption profiles. The characteristic mono-, bis- and tris- complex peak were found to be located at 600 nm, 541 nm and 492 nm, respectively. The areas of the characteristic peaks were converted into the relative fractions by normalizing them to the maximum area-value for each characteristic peak. As no constraints on the sum of fractions were imposed in the modeling of the data, it was used to validate the quality of the found models (Figure S5b). The sum of fractions is close to 1 at all pH values except at pH 1, indicating that at low pH values not all  $\text{Fe}^{\text{III}}$  ions are cross-linked to TA. This is in line with what previously has been reported in similar systems<sup>11</sup> and it can be explained by the electrostatic repulsion between the positively charged polymer and the iron aqua complexes at low pH.

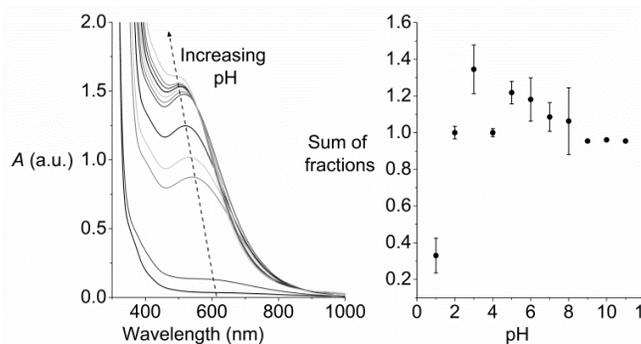


Figure S5. a) UV/VIS absorption profiles of solutions of Fe<sup>III</sup>/TA/PAA at pH values from 1-12. The arrow points in the direction of increasing pH. b) The sum of fractions plotted as a function of pH. When no standard deviation can be seen it is smaller than the size of the points.

### Dynamic oscillatory rheology

The mechanical properties of the hydrogels were investigated by performing dynamic oscillatory rheology experiments using an Anton Parr MCR 501 Rheometer equipped with a parallel plate geometry and an evaporation hood (diameter of rotating top plate: 25 mm).

The mechanical properties were assessed by performing frequency sweeps in the linear viscoelastic range (LVR) at a strain of 15 % (LVR is 0-30 % strain for a pH 12 hydrogel (Figure S6)) while monitoring the storage ( $G'$ ) and loss modulus ( $G''$ ). The experiments were performed at 20 °C. Hydrogels were allowed to rest for 1 h prior to the rheology experiments.

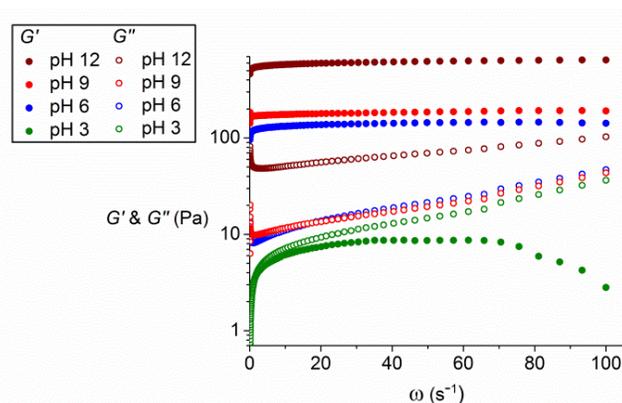


Figure S6. a) Storage ( $G'$ ) and loss ( $G''$ ) modulus as a function of angular frequency for four pH values.

### SAXS

The static SAXS measurements were performed on the modified SAXS NanoSTAR camera (Bruker-AXS GmbH, Germany) in transmission geometry at Aarhus University, Denmark.

The apparatus was equipped with a Bruker AXS HI-STAR two-dimensional position sensitive gas detector. Diluted solutions of Fe<sup>III</sup>/TA/PAA was created (~ factor 13 lower than the original hydrogel recipe, TA and PAA concentration of 1.1 mg/mL and 10 mg/mL, respectively, pyrogallol to Fe<sup>III</sup> molar ratio of 3:1). The pH was increased by titration with a small volume of NaOH to the requested values. The samples were transferred to precalibrate home-made quartz capillaries (Diameter: 2 mm, wall thickness: 0.010 mm). Each sample was measured at 20 °C for 30 minutes (Figure S7).

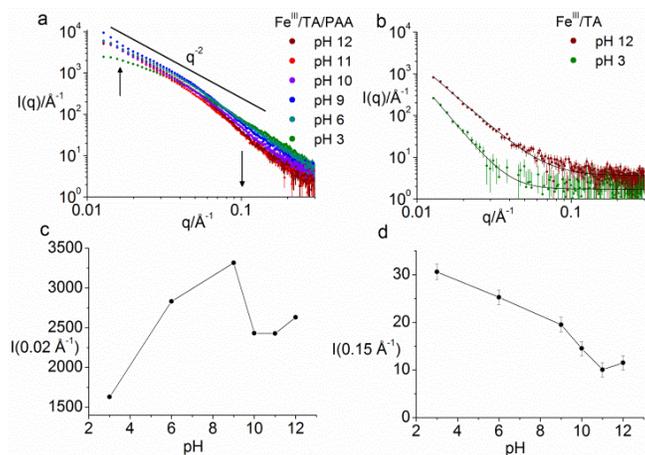


Figure S7. SAXS data. Intensity profiles for a)  $\text{Fe}^{\text{III}}/\text{TA}/\text{PAA}$  and b)  $\text{Fe}^{\text{III}}/\text{TA}$ . c) and d) are  $I(0.02 \text{ \AA}^{-1})$  and  $I(0.15 \text{ \AA}^{-1})$  plotted as a function of pH for  $\text{Fe}^{\text{III}}/\text{TA}/\text{PAA}$ .

### Competitive binding with EDTA

The gel reversibility was tested by competitive binding with EDTA (Ethylenediaminetetraacetic acid, Sigma Aldrich, CAS no. 60-00-4). Hydrogels (half the volume of the original recipe: 75  $\mu\text{L}$ ) with a pH of 6, 9 and 12 were immersed in 1/2 mL 150 mM EDTA (pH 5). The samples were shaken during the first 10 minutes and then allowed to rest (Figure S8)

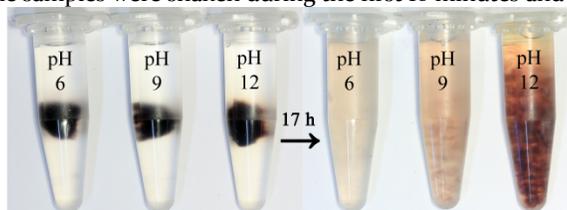


Figure S8. Test of the gel reversibility by competitive binding using EDTA.

### SEM images of threads

SEM images of threads were obtained using an FEI Nova600 SEM (FEI, Eindhoven, The Netherlands) using secondary electrons at 5 keV (Figure S9).

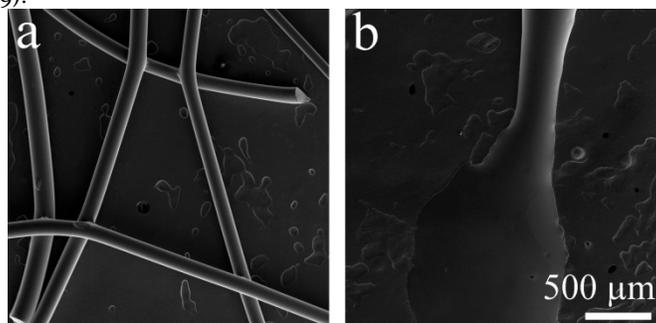


Figure S9. SEM images of  $\text{Al}^{\text{III}}/\text{TA}/\text{PAA}$  threads that have been a) dried immediately after extracting them and b) has been swollen by a drop of water prior to drying. The scale bar is shown in (b).