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## Methods

### Synthesis of DOPA-PAA, DOPA-chitosan and hydrogels

DOPA-polyallylamine (DOPA-PAA) with a grafting density of ~9.5% and DOPA-chitosan with a grafting density of ~3.3% was synthesized according the previous published protocol[1]. To prevent solubility issues, a chitosan oligosaccharide version was employed, which due to its shorter chain length allows for easier dissolution than other chitosan versions (Sigma Aldrich, Cas no. 148411-57-8a, average MW of 5000 Da). In agreement with work by Lee *et al*. we found that the solubility of chitosan was greatly enhanced as a result of the DOPA-grafting, allowing more concentrated hydrogels to be synthesized[2]. The grafting was verified using $^1$H NMR, FTIR and UV/VIS absorption. The $pK_a$ values of the polymers were obtained by potentiometric titration with NaOH as the titration agent in 0.1 M KCl at room temperature under nitrogen atmosphere. The titration was performed using a Metrohm 809 Titrando equipped with a calibrated Metrohm Solvotrode and a mechanical Metrohm 802 stirrer (Metrohm AG, Herisau, Switzerland). DOPA-PAA based hydrogels were likewise synthesized following a previous published protocol but using $AlCl_3 \cdot 6H_2O$, $Ga(NO_3)_3 \cdot 3H_2O$ and $InCl_3 \cdot 3H_2O$ as metal sources (Sigma Aldrich, CAS no. 7784-13-4, 69365-72-6 and 22519-64-8, respectively). In brief, 22.5 mg DOPA-PAA was dissolved in 75 µL 0.55 M NaOH. The polymer solution was mixed with 25 µL 136 mM $M^{III}$ solution to establish a 3:1 catechol:$M^{III}$ ratio. Finally, the hydrogel was established by increasing the pH with 50 µL NaOH with a concentration adjusted to obtain the desired final pH of the hydrogel. The polyallylamine:$M^{III}$ reference samples for the rheology experiments where prepared according to the hydrogel protocol but with polyallylamine replacing DOPA-polyallylamine. The $Fe^{III}$:DOPA-chitosan hydrogels were created by dissolving 33.75 mg DOPA-chitosan (1.5 times the mass used in the DOPA-PAA based gels) in 75 µL demineralized $H_2O$. The polymer solution was mixed with 25 µL 73 mM $Fe^{III}$ solution to establish a 3:1 catechol:$Fe^{III}$ ratio. Finally, the hydrogel was established by increasing the pH with 50 µL NaOH with a concentration adjusted to obtain the requested final pH of the hydrogel.

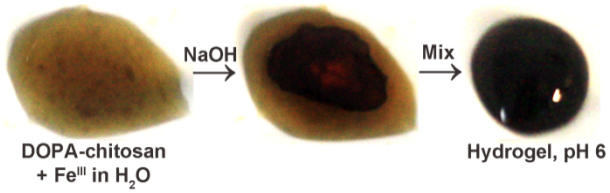


**Fig. S1** Hydrogel formation of $Fe^{III}$:DOPA-chitosan hydrogel. To the left a green liquid containing DOPA-chitosan and $Fe^{III}$ ions is shown. The green color can be assigned to the formed mono-species at low pH. After addition of base three different colors can be observed (red, blue, green), which follows the gradient in pH going from high to low from the center to the edge. Finally, the components are mixed and a homogenous hydrogel is formed.

### 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: 8 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 DOPA-PAA based hydrogel (Figure 2b)), while monitoring the storage modulus (*G'*). The experiments were performed at 20 °C. We used the ungrafted polymer as reference for all systems except $Fe^{III}$-*g*-DOPA-chitosan for which the low solubility of the ungrafted chitosan impeded rheological measurements of the reference material. The self-healing properties were investigated by straining the gels from 0-400 % strain at a frequency of 1 $s^{-1}$. Afterwards the recovery of the materials was assessed by monitoring the storage modulus at 1 $s^{-1}$ and an amplitude of 1% strain.

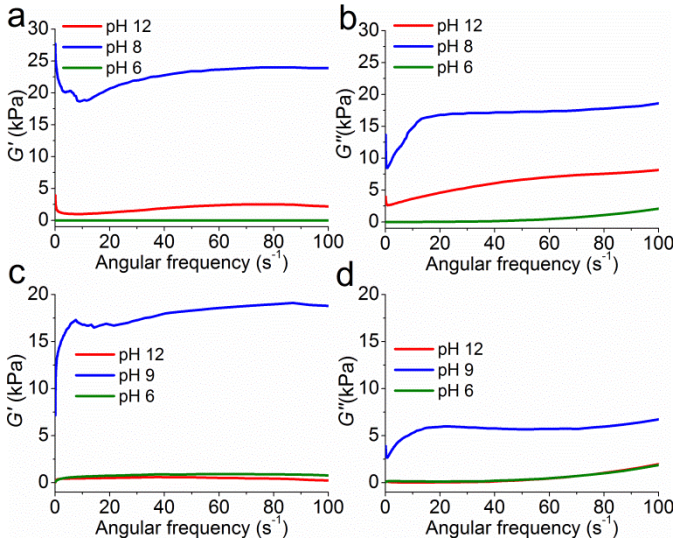


**Figure S2: Frequency sweeps. (a) Storage and (b) loss modulus** for $Fe^{III}$:DOPA-chitosan hydrogels at pH 6, 8 and 12. (c) Storage and (d) loss modulus $Al^{III}$:DOPA-PAA hydrogels at pH 6, 9 and 12. The same trend was obtained for the $Ga^{III}$ and $In^{III}$ cross-linked DOPA-PAA gels.

**UV/VIS absorption**

6 mL stock solution of $M^{III}$ ($M^{III}$: $Fe^{III}$/$Al^{III}$/$Ga^{III}$/$In^{III}$) and DOPA-chitosan or DOPA-PAA in 0.1 M HCl was prepared with a $M^{III}$ to DOPA ratio of 1:3 (DOPA concentration of 1 mM for the titration with DOPA-chitosan and 0.4 mM for the titration with DOPA-PAA). The pH was gradually increased by titration with NaOH, while the pH was monitored with a Metrohm pH meter equipped with a Metrohm unitrode. The pH was increased in steps of one units from pH 1 to a final pH of 12 and the spectral changes were monitored by performing UV-VIS absorption measurements at every step using a UV-Visible absorption spectrophotometer (PerkinElmer lambda 25) equipped with quartz cuvettes (path length: 1 cm). To investigate whether irreversible cross-links had formed as a result of pH catalyzed quinone tanning (Scheme 1a, e, f) the pH was reduced to 1 with 1 M HCl after having reached pH 12. The absorption profiles were collected from 200-500 nm at ambient temperature (Figure 1a and 5a).

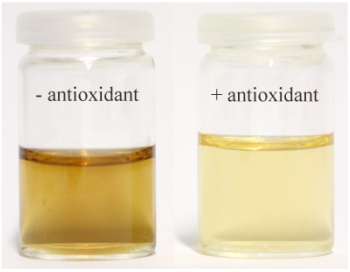


**Figure S3:** $Al^{III}$:DOPA-polyallylamine solution at pH 12 without and with 0.1 M ascorbic acid after 5 hours of mixing.

**EXAFS**

The gallium K-edge EXAFS spectra of $Ga^{III}$ cross-linked DOPA-polyallylamine polymers were collected in fluorescence mode at the I811 MaxLAB beam line (Lund, Sweden). The samples were mounted between two Kapton-tape-foils and then placed in a cryostat, which had been cooled to 100 K to minimize thermal vibrations during the measurements. 25 consecutive scans were performed on each sample to improve data

statistics. The raw EXAFS spectra were merged in the software Athena Version 0.8.056. The rest of the data analysis (background correction, normalization, conversion to *k*-space, Fourier transformations) was performed in WINXAS according to the standard data analysis procedure. Fourier transformation of the $k^3$-weighted $\chi(k)$ EXAFS oscillation from $k(Å^{-1})$ space to $R(Å)$ space was performed in a range of $k$ = 1.5 to 9 to obtain a radial structural function in *R* space. In addition, the spectra were Fourier refined to remove data not associated with the first and second coordination shell. The radial distribution functions shown in Figure 3b has been internally calibrated to a Ga-O bond length of 1.984(6) Å, which is the average bond length reported for another $Ga^{III}$:catechol compound[3].

**NMR Spectroscopy**

$^1$H NMR experiments were performed on a Varian Mercury Plus 400 NMR spectrometer (9.4 T) employing a 5.0 mm probe. The samples were prepared by dissolving 27.6 mg DOPA-PAA in 1 mL 0.01 M DCl. 31 µL 0.173 M $AlCl_3$ was added to obtain a 3:1 DOPA to $Al^{III}$ ratio. The pH was adjusted by adding small volumes of concentrated NaOD and the solution was filled into the NMR glass tube to a total volume of ~1 mL. All experiments were recorded using a relaxation delay of 5 s and a pulse flip angle of 45° for an rf-field strength of 25.0 kHz. The experiments further used 32 scans, a spectral width of 6406.1 Hz (16.00 ppm), and an acquisition time of 2.558 s.

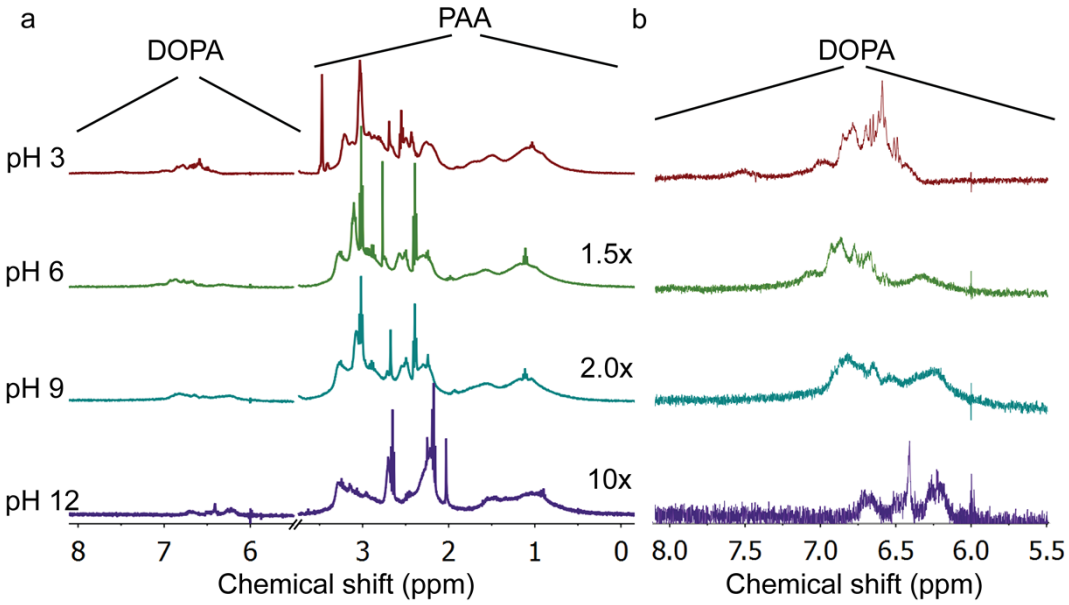


**Figure S4**: Liquid-state $^1$H NMR spectra recorded at 25 °C on $Al^{III}$:DOPA-PAA in $D_2O$ with a final pH of 3, 6, 9 and 12. The pH was regulated using small volumes of concentrated DCl/NaOD. (a) Overview spectra from 0 – 8 ppm, showing the signals from DOPA and PAA. (b) Zoom-in on the $sp^2$ region, which contains the DOPA signal.

The pH values of the solutions was calculated using the following equations[4]:

$$pH = 0.929 \cdot pH^* + 0.41$$

Here $pH^*$ is the direct reading in the $D_2O$ solution of the $H_2O$ calibrated pH-meter.

**Competitive binding with EDTA**

The gel reversibility was tested by competitive binding with EDTA (ethylenediaminetetraacetic acid, Sigma Aldrich, CAS no. 60-00-4). $M^{III}$:DOPA-PAA hydrogels (half the volume of the original recipe: 75 µL) with a pH of 6, 9 and 12 were immersed in 1½ mL 150 mM EDTA (pH 5). The samples were shaken during the first 10 minutes and then allowed to rest (Figure S5).

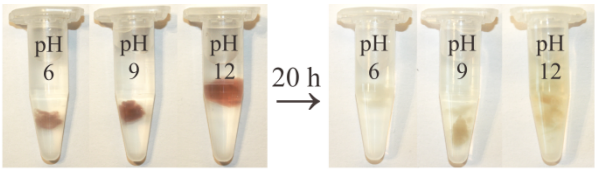


**Figure S5:** Test of the gel reversibility by competitive binding using EDTA (Here shown for $In^{III}$ cross-linked gel).

References

1. M. Krogsgaard, M. A. Behrens, J. S. Pedersen and H. Birkedal, *Biomacromolecules*, 2013, **14**, 297-301.
2. K. Kim, J. H. Ryu, D. Y. Lee and H. Lee, *Biomaterials Science*, 2013, **1**, 783-790.
3. B. A. Borgias, S. J. Barclay and K. N. Raymond, *J. Coord. Chem.*, 1986, **15**, 109-123.
4. A. Krężel and W. Bal, *Journal of Inorganic Biochemistry*, 2004, **98**, 161-166.