

## Supporting Information for

### **Robust hydrogels from catechol rich polymers**

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**Supporting information:** Includes details of catechol grafting protocol and characterization of resulting polymers, rheological profiles of the hydrogels formed by coordinative and covalent cross linking, videos of load-bearing and self-healing of the gel.

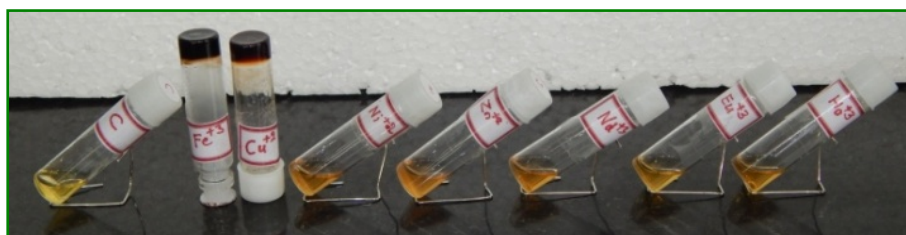
**S1.a. Reductive amination of amine polymers with catechols:** 2 g of chitosan as a representative example (~13 mmol glucosamine repeat units) was dissolved in 40 mL of 1% aqueous Acetic acid solution (pH ~5.0). After complete dissolution of chitosan, 2 mL of glacial acetic acid was further added to the reaction mixture followed by a solution of DHB in 40 mL water and 20 mL methanol. The reaction mixture developed yellowish-brown color as soon as DHB solution was added to the chitosan solution, and the color intensified upon stirring. The reaction mixture was stirred at ambient temperature to allow the formation of Schiff base. The degree of derivatisation (DoD) could be effectively controlled by varying the amount of DHB added, as well as by altering the time of stirring, as detailed in Table S1. Later, solid NaBH<sub>4</sub> was added in small portions under vigorous stirring until the reaction mixture became a white suspension. At the resulting pH of 8.0, the polymer precipitated out. Excess water was carefully decanted to minimize the amount of HCl needed to quench the residual NaBH<sub>4</sub> and to further acidify the reaction mixture. Solution pH was made to 5.0 by addition of HCl causing the product to dissolve and yield a clear solution. The resultant

materials were extensively dialyzed against dilute HCl (0.5 N) for 6 h and with 0.5% acetic acid for 2 h. These solutions were lyophilized prior to use.

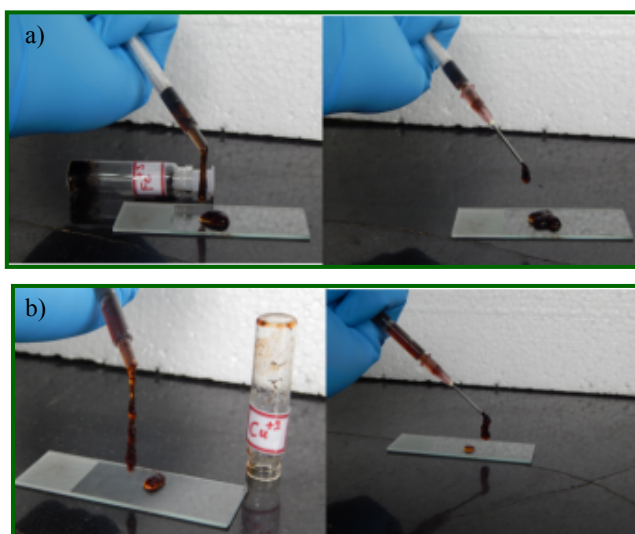
## S2. Calculation of DoD's by $^1\text{H}$ NMR:

For all the polymers, the DoD was calculated from the  $^1\text{H}$  NMR spectra of the polymers by comparing the signal intensity of the aromatic protons with that of the C2 protons in the derivatized and underivatized glucosamine ring. The internal methyl protons of *N*-acetyl moieties of chitosan were taken as the secondary standard for integration.

$$\text{DOD \%} = \frac{1/3 \times \text{Signal intensity due to aromatic protons}}{\text{Signal intensity due to C2 protons}} \times 100$$



*Figure S1.* Digital image of the aqueous solutions of  $\text{Cat}_{\text{C66}}$  in 1% acetic acid, 12 h after addition of various metal ions (metal:catechol = 1:2). The preferential ability of Fe(III) and Cu(II) ions to induce gel-formation can be clearly observed. Vial marked C represents the control (2% w/v chitosan solution in 1% acetic acid containing same amount of Fe(III) ions).



*Figure S2.* Injectable gels formed at  $\text{pH} = 3$  upon addition of a) Fe(III) and b) Cu(II) ions to  $\text{Cat}_{\text{C66}}$  polymer (metal:catechol = 1:3). In each panel, the image on left shows the use of syringe without needle to extrude the gel while the image on right is that of a syringe fitted with 19 gauge needle for extrusion of the gel.

### 3. Rheology:

#### S3.1. Effect of DoD on the rheological response of the Fe(III)-hydrogels:

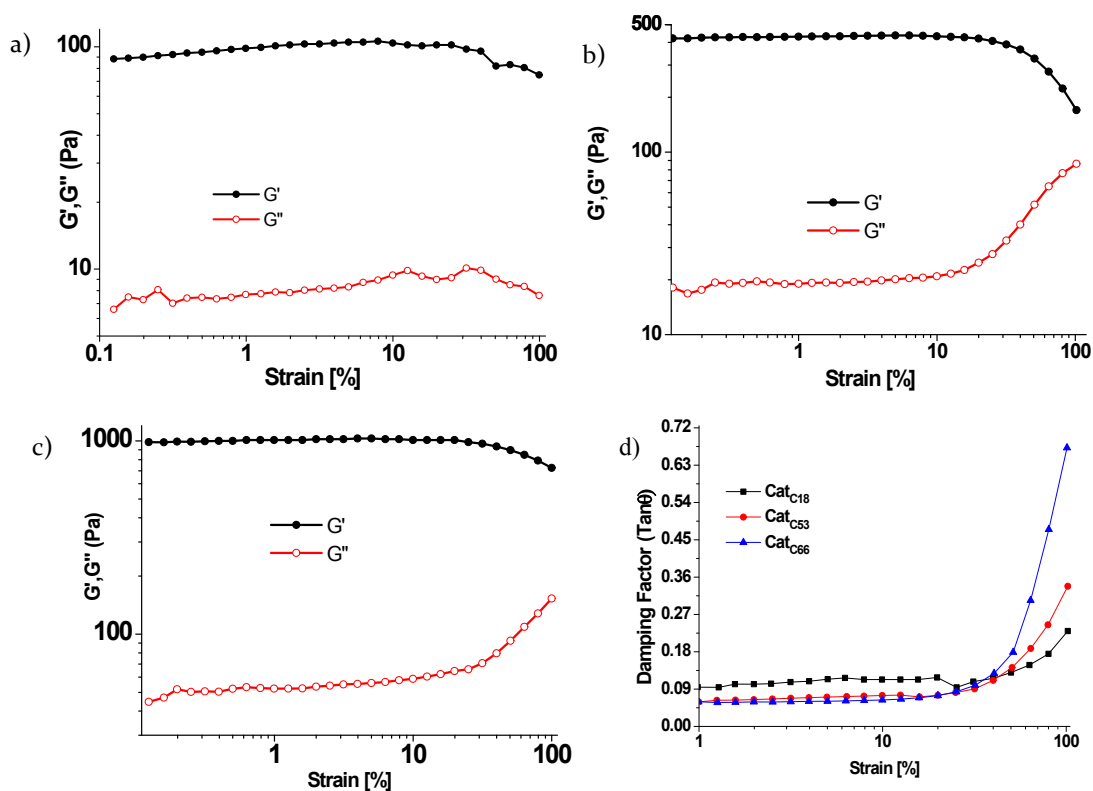
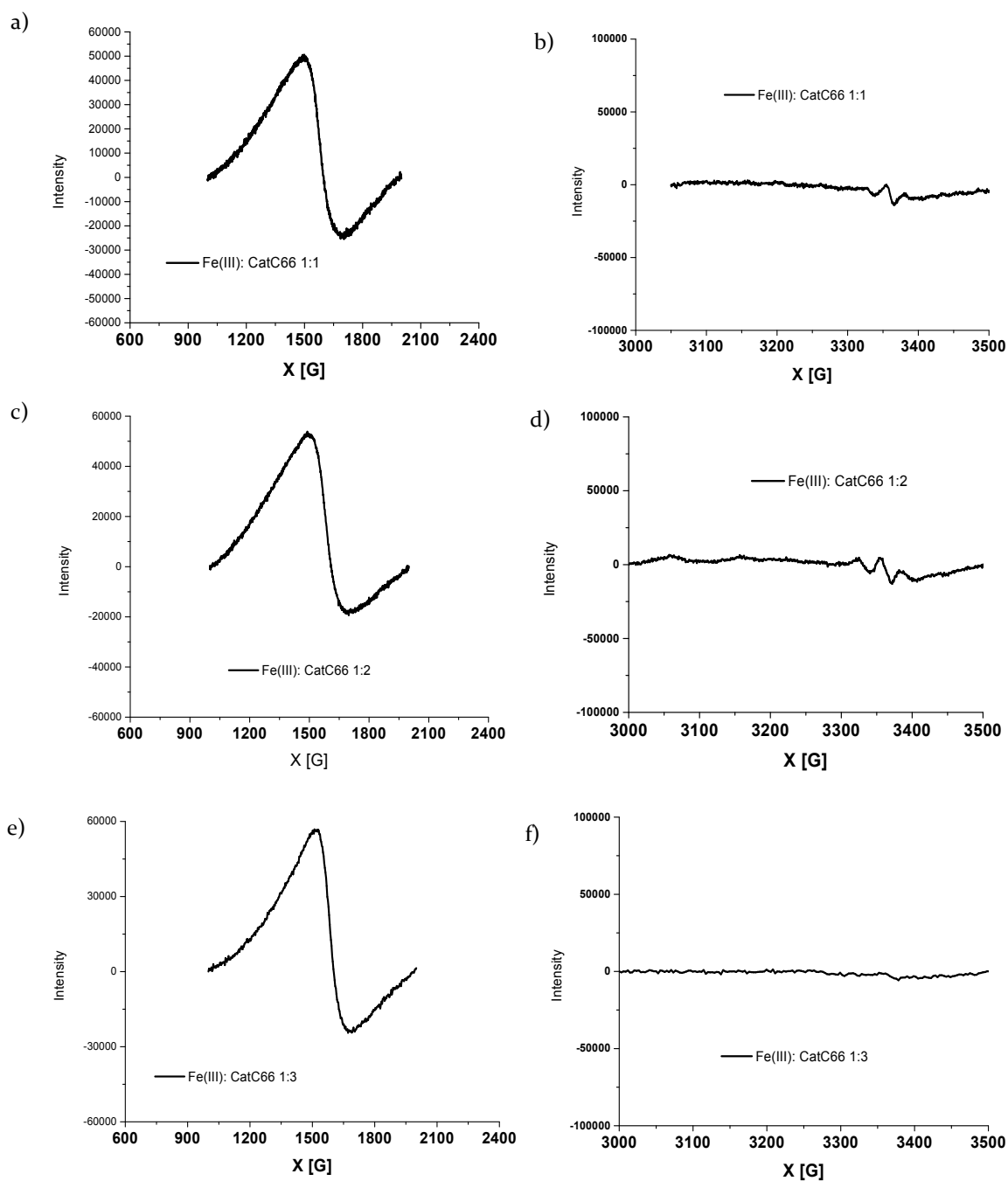


Figure S3. Rheological profiles of the hydrogels prepared at Fe(III):catechol = 1:2 from a) Cat<sub>C18</sub>, b) Cat<sub>C53</sub> and c) Cat<sub>C66</sub>, showing the effect of DoD on the mechanical profiles of gels. d) Damping factor ( $\tan\theta = G''/G'$ ) of these gels, indicating enhanced strength and a relative decrease in elasticity on increasing catechol derivatization (DoD).



*Figure S4.* EPR spectra of the xerogels prepared using Cat<sub>C66</sub> at varying coordination ratios (Fe(III):catechol). a,b: coordination ratio = 1:1; c,d: coordination ratio = 1:2, e,f - coordination ratio = 1:3. The peak formed at 1400-1600 G (peak A) is indicative of the formation of Fe(III)-catechol complexation and the peak at 3300-3400 G (peak B) corresponding to Fe(II)-semiquinone formation (observed only in the gels formed at higher concentrations of Fe(III), i.e. at Fe(III):Cat<sub>C66</sub> = 1:1 and 1:2).

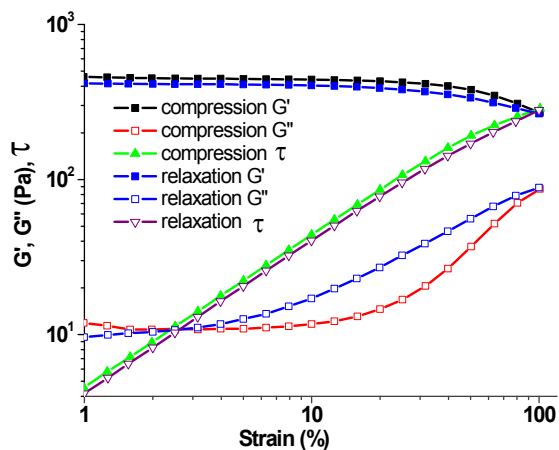


Figure S5. Rheological profiles of the **Fe-Gel** upon application followed by removal of stress. Highly reproducible profiles can be observed indicating significant recovery of gel was observed immediately upon removal of stress.

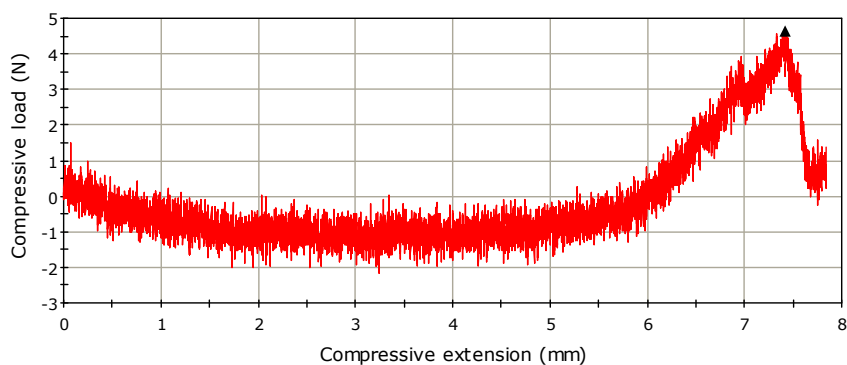


Figure S6. Load vs Compression profile of the **Fe-Gel** obtained on a UTM. It indicates that the gel was able to take a compressive load of 4.4 N while undergoing a compressive extension up to ~70% of its initial height (10 mm) before undergoing disintegration.

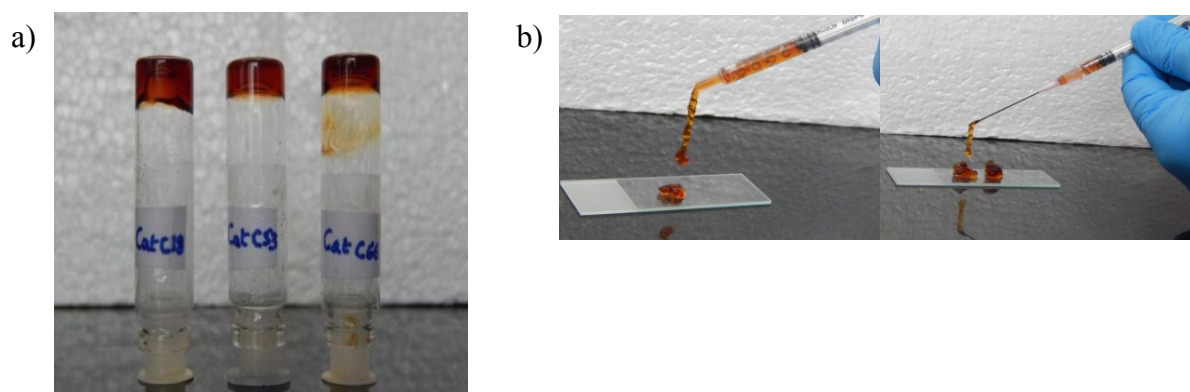


Figure S7. a) Hydrogels formed by  $\text{Cat}_{\text{C18}}$ ,  $\text{Cat}_{\text{C53}}$  and  $\text{Cat}_{\text{C66}}$  upon oxidative cross-linking. (induced by addition of  $10\ \mu\text{L}$  of  $0.2\ \text{M}\ \text{NaIO}_4$  solution to  $500\ \mu\text{L}$  of  $2\% \text{ w/v}$  polymer solutions). b) Injectable gels formed by oxidative crosslinking of  $\text{Cat}_{\text{C66}}$  aqueous solutions ( $\text{pH} \sim 3$ ) by  $\text{NaIO}_4$ . The left image shows use of syringe without needle and right image is of syringe fitted with 19 gauge needle.

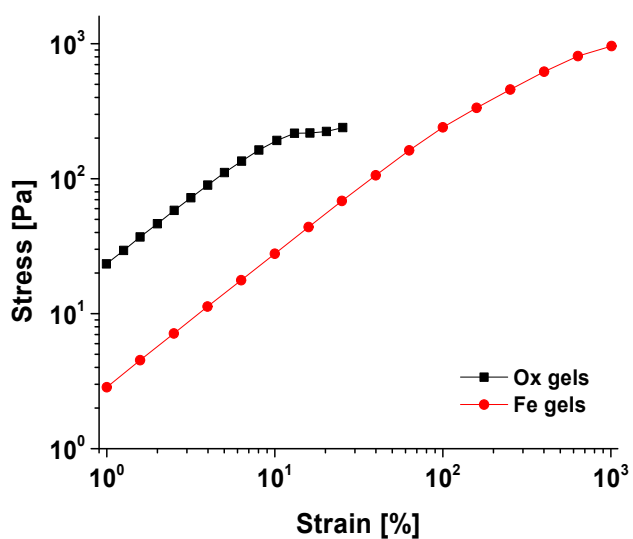


Figure S8. Stress vs strain plot for the **Ox-Gels** in comparison to that of the **Fe-Gels**. The linear elastic response of the oxidatively crosslinked gels was observed only up to 10% strain which is about ten times less than that observed for the **Fe-Gels**. Note the log-log scale.

*Table S1.* Summary of the conditions employed for achieving various degrees of catechol derivatizations.

<b>Polymer</b>	<b>Eqv. of DHB added, (time of stirring)</b>	<b>DoD* (%)</b>
Cat <sub>C18</sub>	7 mmole, 0.53 eqv, (1 h)	18
Cat <sub>C53</sub>	50 mmole, 3.84 eqv, (3 h)	53
Cat <sub>C66</sub>	50 mmole, 3.84 eqv, (3.5 h)	66
Cat <sub>C80</sub>	65 mmole, 5 eqv, (5 h)	80

\*DoD = Degree of derivatization, estimated from <sup>1</sup>H NMR spectra (see section S2).

*Table S2.* Effect of DoD on the kinetics of gelation in presence of Fe(III)

<b>Polymer<sup>a</sup></b>	<b>Time for gelation<sup>b</sup></b>
Cat <sub>C18</sub>	9 h
Cat <sub>C53</sub>	15 min
Cat <sub>C66</sub>	5 min

<sup>a</sup> at 2% w/v concentration in 1% aqueous acetic acid.

<sup>b</sup> at Fe(III):catechol = 1:2.6

*Table S3.* Minimum Fe(III):catechol ratio and time required for gelation at this Fe(III):catechol ratio.

<b>Polymer<sup>a</sup></b>	<b>Minimum Fe(III):cat</b>	<b>Time for gelation</b>
Cat <sub>C18</sub>	1:2.6	9 h
Cat <sub>C53</sub>	1:5	9 h
Cat <sub>C66</sub>	1:22	1.5 h

<sup>a</sup>at 2% w/v concentration in 1% aqueous acetic acid.