**Supporting Information of**

**Soft Dynamic covalent Hydrogel based on Iron(II)Tetraphenylporphyrinato-Functionalized 4-Arm Poly(ethylene oxide)**

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**General**

**Materials**  
THF (99.5%, J.T. Baker, The Netherlands), was purified by distillation from calcium hydride and stored in glass vessels over sodium benzophenone.  
DMF (99%, Sigma-Aldrich France), Iron (II) Chloride, (99%, Sigma-Aldrich France), potassium hydride (30 wt. %, dispersion in mineral oil, Sigma-Aldrich France), α,α′-dichloro-m-xylene (98%, Fluka), poly (ethylene glycol) Mn=20000 (Mn_app = 16218, Ip=1.06) Mn_mn= 17800 (Creative PEG Works, Winston Salem USA), were used as received.

**Characterization**

1H NMR spectra were recorded in CDCl₃ on a Bruker 400MHz apparatus. SEC analysis was performed in tetrahydrofuran (THF) (1 ml / min) or dimethyl formamide (DMF) (0.5 ml/min, 60°C), on a Waters apparatus equipped with a refractive index/photodiode array 2996 dual detection equipped and fitted with three TSK columns (1 500, 10⁴, 10⁵ Å °). The polymer molar masses were determined by SEC using linear poly(ethyleneoxide) as calibration standards. A trace of trichlorobenzene added to the sample was used as the internal flow marker reference.

UV-Vis spectra were recorded on a Varian Cary 3E spectrophotometer.

**5-(4-Hydroxyphenyl)-10, 15, 20-triphenyl-porphyrin (1)**

This compound was synthesized according to the literature as described in ref.:  

1HNMR (400MHz, CD₂Cl₂): δ -2.9(br s,2H,NH), 1.2(t,6H, CH₃), 2.17(br,2H, CH₂), 3.56(br,2H, OCH₂), 3.69(br,2H, OCH₂), 4.26(t,2H, PhOCH₂), 4.83(t,1H, acetal), 7.22(d,2H, H₃,5 Ar), 7.69(d,6H, H₃,5 Ar), 8.04(d,2H, H₂,6 Ar), 8.14(d,6H, H₂,6 Ar), 8.77(bd,6H, Hβ,pyr), 8.82(d,2H, Hβ,pyr).
Figure S1: Chemical procedure to obtain ω-Fe(III)Cl meso-tetraphenyl porphyrinato functionalized 4-Arm Poly(ethylene oxide):

Tetra chlorobenzyl functionalized 4-Arm Poly(ethylene oxide) (2)

4-Arm Poly (ethylene glycol) tetrahydroxy terminated (10g, Mw= 20000) were dissolved in anhydrous THF (100 mL). Potassium hydride (0.1g, 2.5mmol), was added in small portions under nitrogen. The mixture was vigorously stirred for 24 h at room temperature before addition of α,α-dichloro-m-xylene (8g, 46 mmol). The temperature was increased at 50°C and the mixture was vigorously stirred for 24 h under vacuum.

After addition of methyl alcohol (3ml), the solution was evaporated to dryness. The polymer was dissolved in dichloromethane (100mL), the organic phase was washed with water (3 x 100 mL), dried with magnesium sulfate, filtered, and concentrated under vacuum. The product (2) was finally recovered and purified twice by precipitation in diethyl ether. After filtration the product was dried under vacuum Yield: 10g. SEC: Mn_{app} = 16595 Ip= 1.06. ^1H NMR is given in figure S2.
Preparation of ω-(meso-tetraphenyl porphyrinato) functionalized 4-Arm Poly(ethylene oxide) (3). Compound (2) (1 g, 0.05 mmol) was dissolved in dry DMF (20 mL) with 5-(4-Hydroxyphenyl)-10, 15, 20-triphenyl-porphyrin (1) (0.2 g, 0.3 mmol) and K$_2$CO$_3$ (0.1 g, 7 mmol) was added. After 36 H at room temperature, dichloromethane (100 mL) was added. The organic phase was washed with water, dried with magnesium sulfate, filtered, and concentrated under vacuum. The polymer (3) was purified twice by precipitation in diethyl ether. After filtration the product was dried under vacuum Yield: 0.5 g. UV/visible (THF): λ (nm): UV/visible (THF), λ (nm): 417; 614; 549; 592; 652. SEC : Mn$_{\text{app}}$ = 19054 Ip=1.07. $^1$H NMR is given in figure S3.

Figure S2: 1H NMR spectrum of Tetra chlorobenzyl functionalized 4-Arm Poly(ethylene oxide) in CDCl$_3$ (2)

Figure S3: 1H NMR spectrum of ω-(meso-tetraphenyl porphyrinato) functionalized 4-Arm Poly(ethylene oxide) in CD$_2$Cl$_2$.
Preparation of £ (Fe(III)Cl meso-tetraphenyl porphyrinato) functionalized 4-Arm Poly(ethylene oxide)(4) To a 4-Arm Poly(ethylene oxide)H$_2$TPP (3) (250mg) in dry DMF (40ml), anhydrous FeCl$_2$ (150 mg) was added and the stirring was stirred at 100°C under N$_2$ atmosphere until complete insertion of the metal was shown by UV/Vis spectroscopy (corresponding spectrum). The resulting solution was diluted with 50 ml of dichloromethane and washed with water several times and concentrated. The product (4) was finally recovered and purified by precipitation in diethyl ether. Yield 0.25g (95%).

UV/visible (THF): $\lambda$ (nm): 370; 419.4; 508.9.
**Preparation of gel.** 100mg of compound 4 is dissolved in 5ml of methylene chloride in a small flask. After evaporation of methylene chloride a red brown film was obtained. Small aliquots of water added progressively lead to the swelling of the film and a color change from red-brown to green attesting to the formation of bis-FeIII μ-oxo-TPP bond. Addition of water is stopped when it was no more absorbed by the hydrogel. A green hydrogel is finally obtained and its final concentration was checked by gravimetry.

The chemical reactions occurring upon addition of water on compound 4 and pH variation are the following:

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\begin{align*}
2 \text{Fe}^{III} \text{ClTPP}_{\text{THF}} + \text{H}_2\text{O} & \rightarrow \text{FeOFe} \text{(TPP)}_2 \quad \text{pH=1} \\
\text{pH>3} & \rightarrow 2 \text{Fe}^{III} \text{ClTPP}
\end{align*}
\]

**Gel acidification.**

Vapor from a 12N HCl bottle were sucked by a pipette, injected in the flask containing the gel and the flask was immediately closed. After a few minutes a color switch from green to red-brown was observed.

**Rheological measuremments**

All experiments were carried out with a stress controlled rheometer (AR2000 from TA-Instruments) with plate-plate geometry (25mm diameter, 1mm gap) in the linear regime (checked by stress sweep done at different frequencies). Temperature was regulated (±0.1°C) by a peltier plate. It was checked that normal forces were relaxed before starting an experiment.
Figure S6: Frequency dependence of the normalized dynamic moduli of acidified hydrogel and hydrogel obtained from (TPP-PEO)$_{4\text{arm}}$ (Without Fe). T=15°C. $G'$ is normalized by the plateau value at high frequencies whereas $G''$ is normalized by the value at its maximum.

The hydrogel that had undergone the treatment with HCl, which leads to the transient network (Fig 2), was kept a few weeks in the fridge before being submitted to NET3 treatment leading to the chemical network, insoluble in organic solvent. The dynamic rheological properties of the resulting hydrogel were again analysed and the results are illustrated below.

Figure S7: Dynamical rheological analysis of the FeCl-TPP-PEO hydrogel after HCl treatment and NET3 treatment
In the frequency range investigated the elastic moduli are invariant (this confirm that the very slight decrease of $G'$ observed at 25°C in Figure 2 results from an artefact). The slight increase of $G'$ that can be observed at 35°C at very low frequencies can be attributed to slight evaporation, despite a thin layer of silicon oil which was deposited on the edges of the sample to limit this phenomenon, thus reinforcing “artificially” the gel.

Interestingly the moduli are higher (3000-4000Pa) instead of 650Pa. this can be due to the fact that this sample was kept in its acidified form a few weeks before being submitted to NEt3, and progressive rearrangement of the structure could occur during this time.

**Comment about the nature of the Fe-TPP complex and Fe-O-Fe Bonds**

The chemical bonds insuring the crosslinking (Fe-Porphyrin complex and Fe-O-Fe ) are not reversible and present a pronounced covalent character This has been shown in literature for the complex$^1$ and for the Fe-O-Fe bond by simple distance calculation according to Shannon$^2$ and the knowledge of the crystallographic structure of the O(FeIII-TPP)$_2$ dimer$^3$: The expected length for Fe-O based on their ionic radii and their coordination is $0.58(R_{Fe}) + 1.35(R_{O}) = 1.93\text{Å}$. Taking account covalent radii, it is $0.72 + 1.21 = 1.93\text{Å}$, therefore the Fe-O bond has a ionic/covalent character. But in μ-Oxo-bis(FeIII-TPP) the iron atom is 0.48 Å out of the plane of the four pyrrole nitrogens toward the oxide atom and the Fe-O bond distance is 1.76 Å, so there is a clear orbital overlap and this tend to reinforce the covalent character of the Fe-O-Fe bond.