Electronic Supplementary Material (ESI) for Polymer Chemistry.

Hybrid organic-inorganic supramolecular hydrogel reinforced with $CePO_4$ nanowires†

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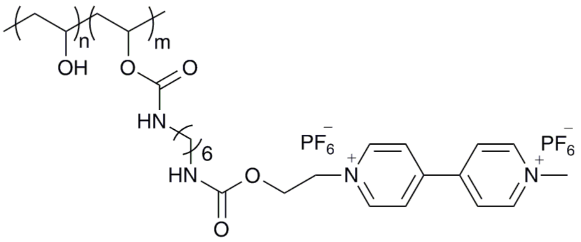
S.1 Synthesis and characterisation of PVA-MV



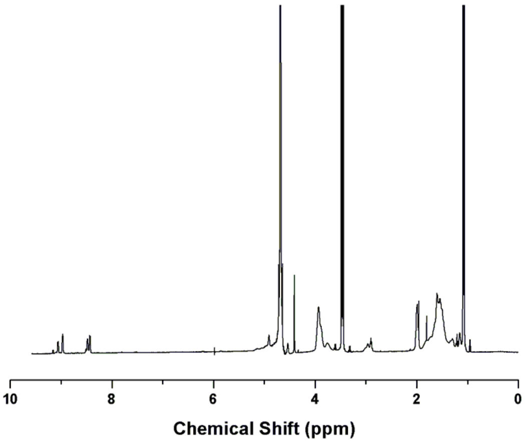


Figure S1: ^{1}H NMR (500 MHz) of PVA-MV.

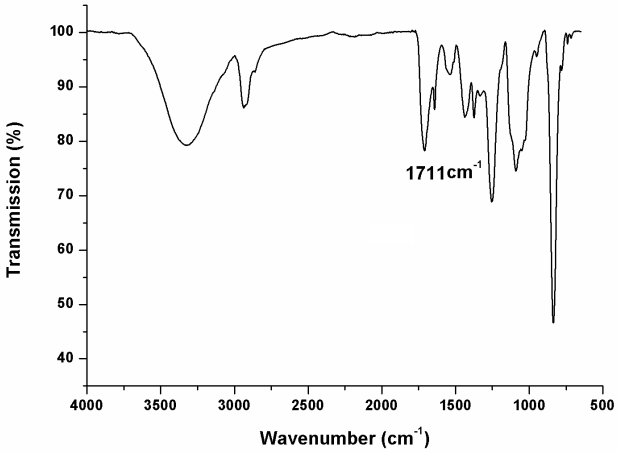
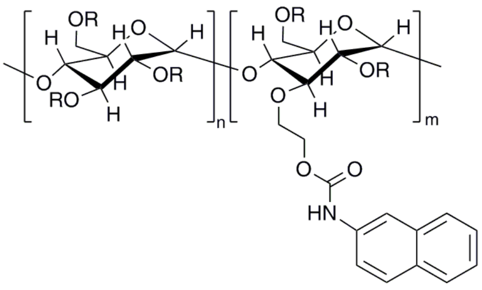


Figure S2: FT-IR characterisation of PVA-MV.

As shown in Figure S1, the signals from 9.17-8.96 ppm and 8.52-8.42 ppm illustrate the viologen group of PVA-MV. Furthermore, The FT-IR characterisation (Figure S2) also demonstrates the functionalisation of PVA from the absorption at 1711 cm^{-1}.

S.2 Synthesis and characterisation of HEC-Np



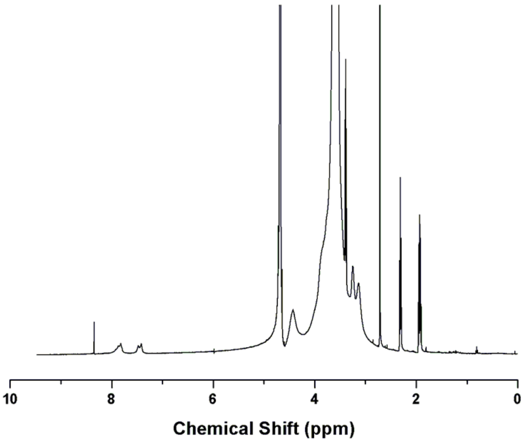


Figure S3: ^{1}H NMR (500 MHz) of HEC-Np.

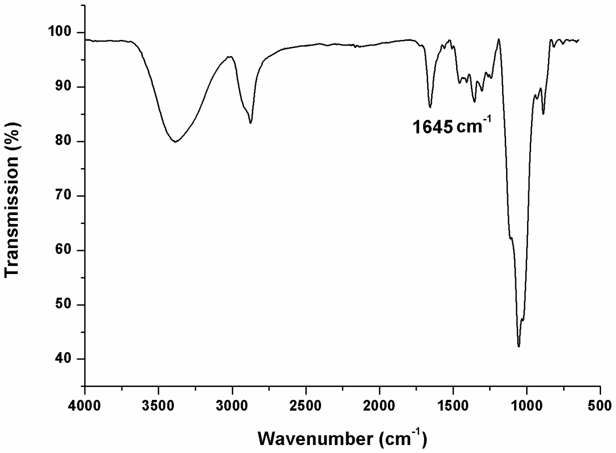


Figure S4: FT-IR characterisation of HEC-Np.

The chemical shift at 7.91-7.35 ppm of Figure S3 indicates the naphthyl group of the HEC-Np product. Moreover, Figure S4 shows the FT-IR spectrums of HEC-Np. The characteristic absorption at 1645 cm^{-1} are attributed to the C=O group of HEC-Np, which can also prove the success of the post reaction.

S.3 Preparation and characterisation of $CePO_4$ nanowire

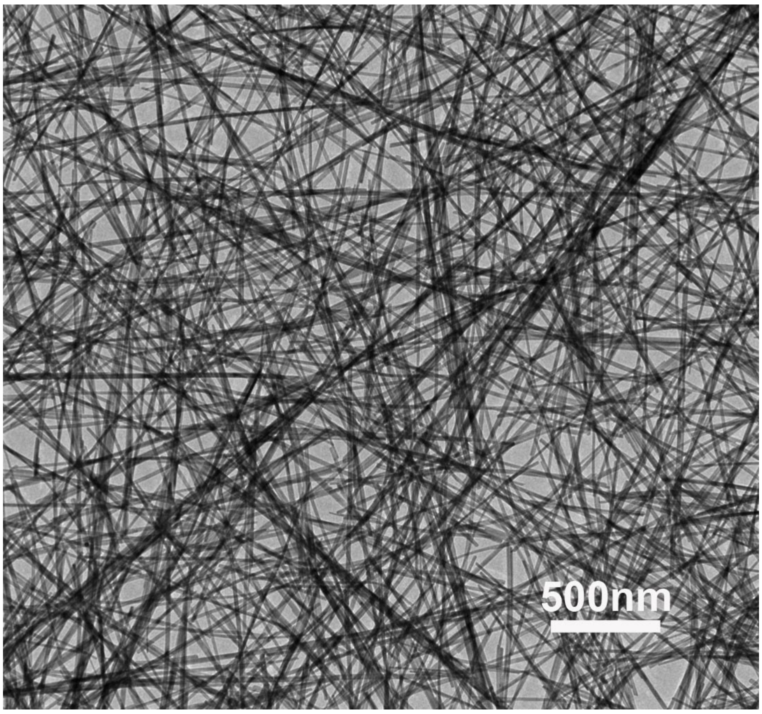


Figure S5: TEM image of $CePO_4$ nanowire.

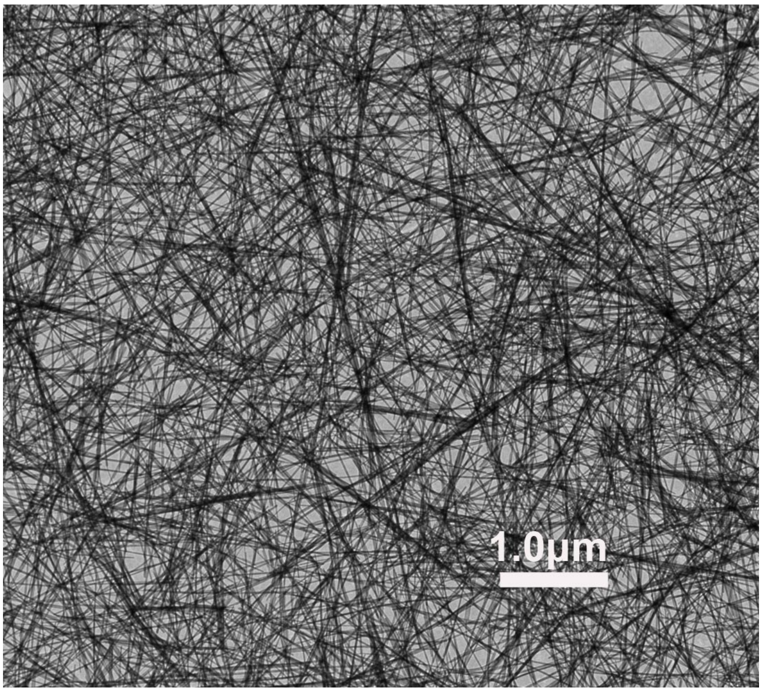


Figure S6: TEM image of $CePO_4$ nanowire.

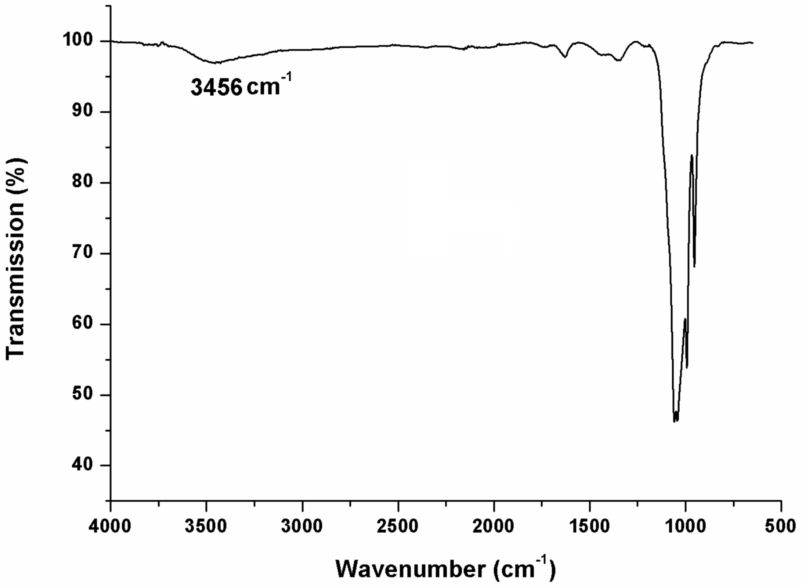


Figure S7: FT-IR characterisation of $CePO_4$ nanowires.

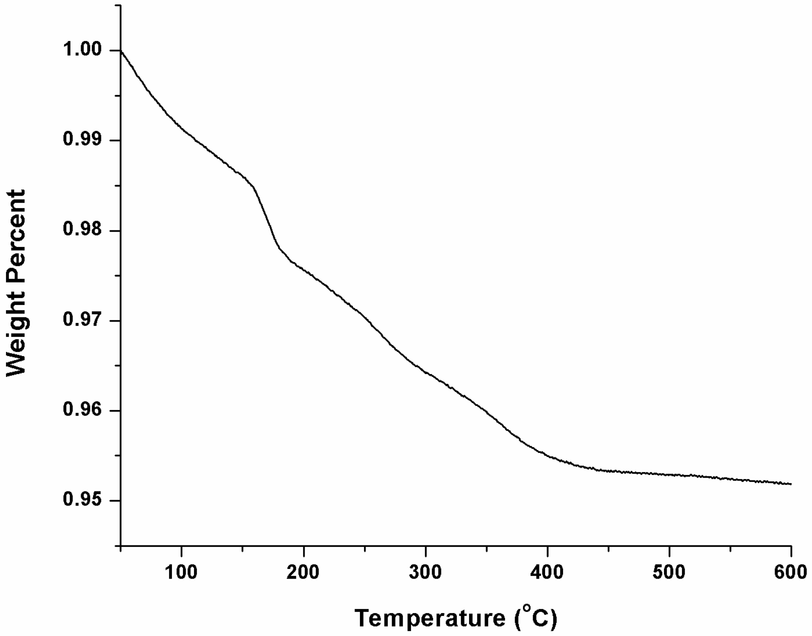
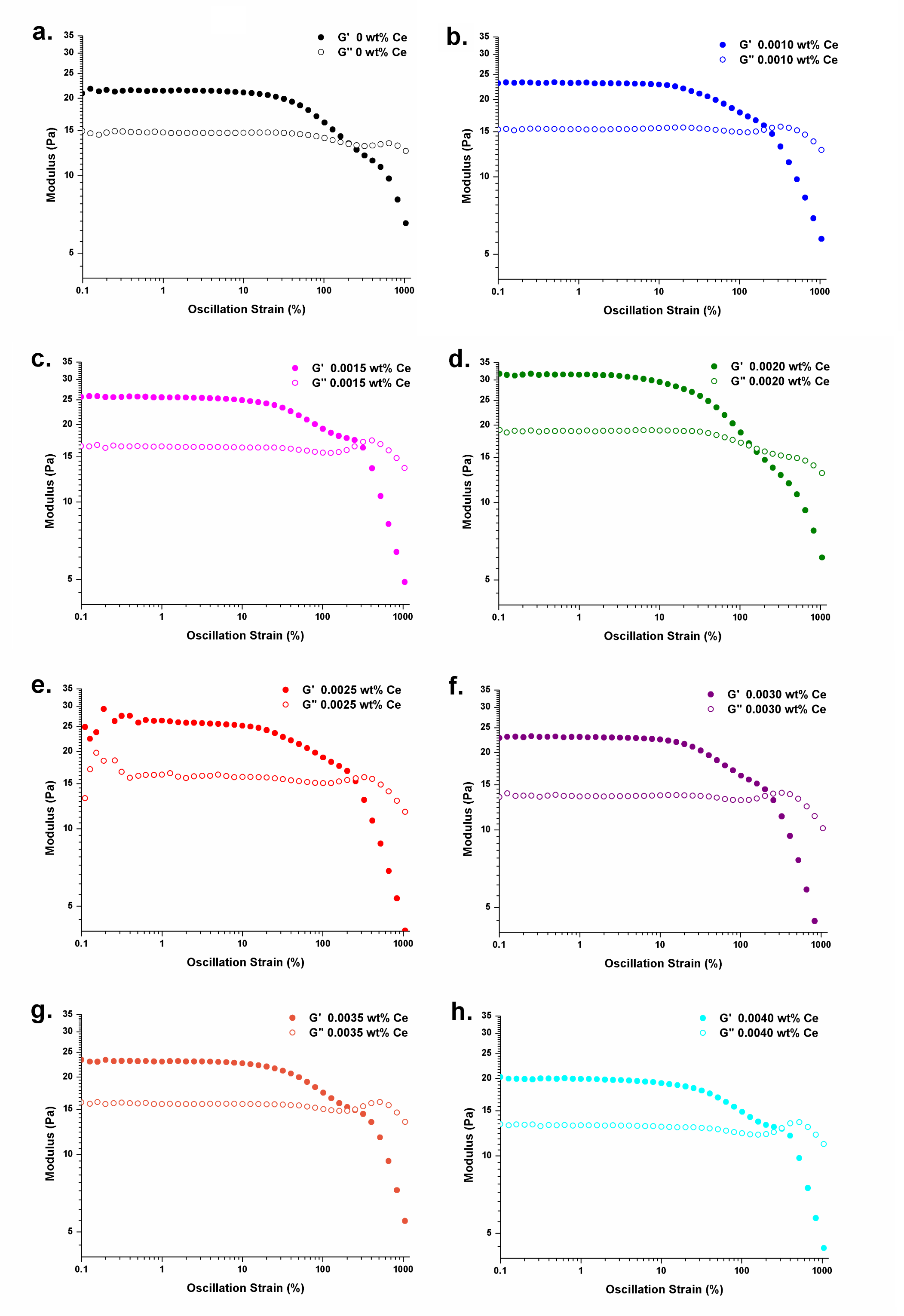


Figure S8: Thermal Gravimetric Analyzer (TGA) results of $CePO_4$ nanowires.

S.4 The rheological characterisation of the hybrid hydrogels with different concentration of $CePO_4$ NWs



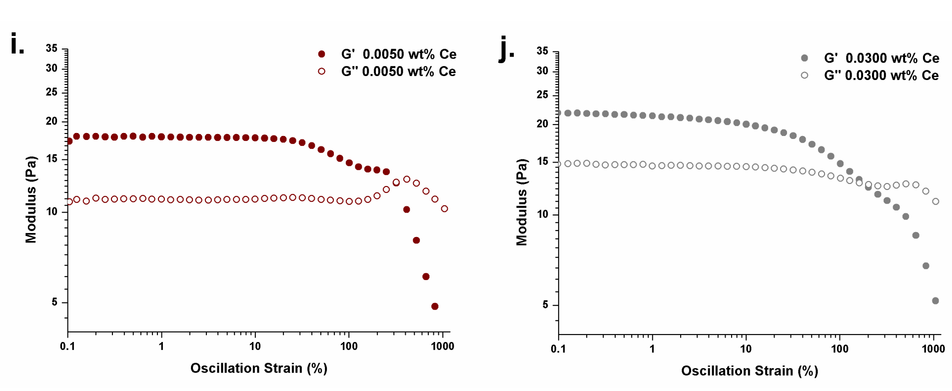
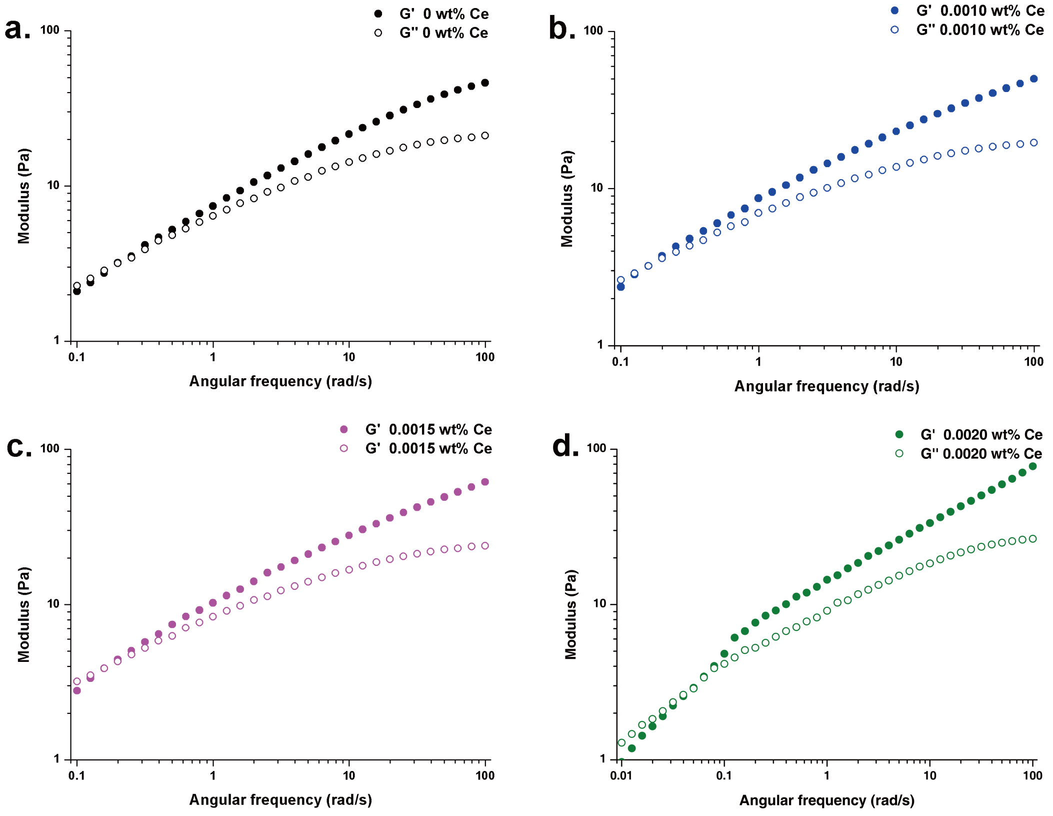


Figure S9: Storage (G') and loss (G") moduli from amplitude dependent oscillatory rheology of $CePO_4$ enhanced hybrid supramolecular hydrogels at 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.05 wt% CB[8] with different concentration of $CePO_4$ NWs. a) 0 wt%. b) 0.0010 wt%. c) 0.0015 wt%. d) 0.0020 wt%. e) 0.0025 wt%. f) 0.0030 wt%. g) 0.0035 wt%. h) 0.0040 wt%. i) 0.0050 wt%. j) 0.0300 wt%. The results demonstrate that the gel with 0.0020 wt% $CePO_4$ NWs have stronger and more ordered networks than others.



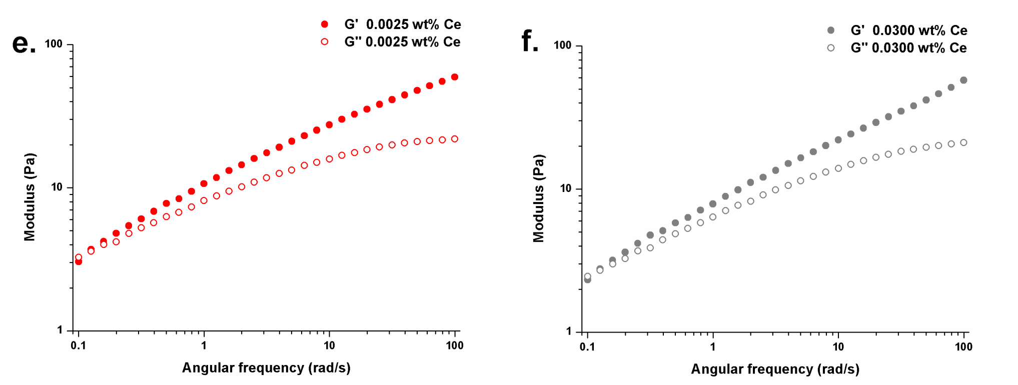


Figure S10: Storage (G') and loss (G") moduli from frequency dependent oscillatory rheology of $CePO_4$ enhanced hybrid supramolecular hydrogels at 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.05 wt% CB[8] with different concentration of $CePO_4$ NWs. a) 0 wt%. b) 0.0010 wt%. c) 0.0015 wt%. d) 0.0020 wt%. e) 0.0025 wt%. f) 0.0300 wt%. The data indicates that 0.0020 wt% $CePO_4$ NWs is the best concentration for this system.

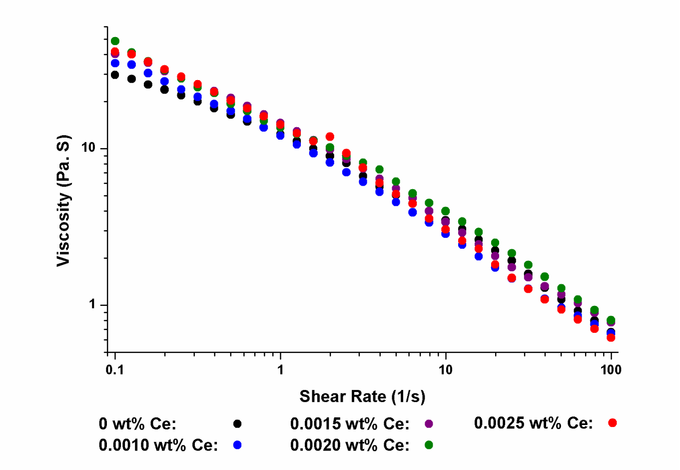


Figure S11: Shear dependent rheology of cerous phosphate enhanced hybrid supramolecular hydrogels at 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.05 wt% CB[8] with different concentration of cerous phosphate NWs, which infers that 0.0020 wt% cerous phosphate NWs system has much stronger internal interactions.

S.5 The SEM characterisation of the hybrid hydrogels with CePO4 NWs aggregates

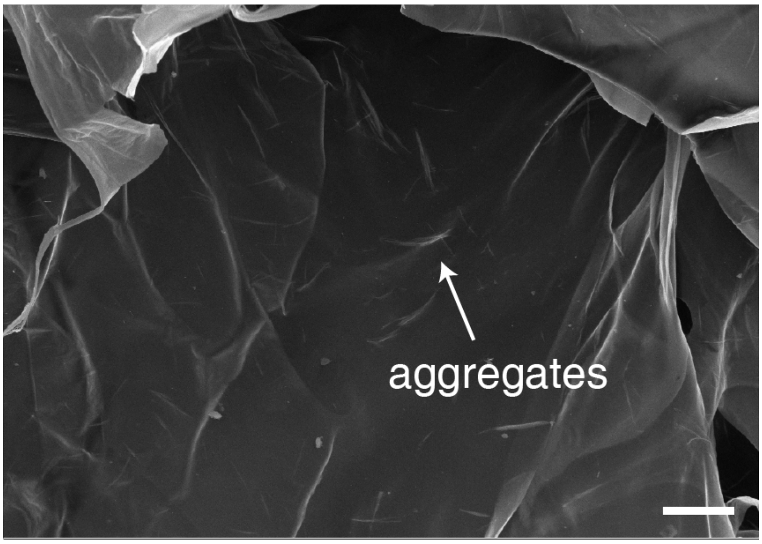


Figure S12: SEM image of cryo-dried and lyophilized samples of hydrogels with 0.0025 wt% NWs, which confirms the NWs aggregates. (Scale bar: 2 μm)

S.6 The control experiment

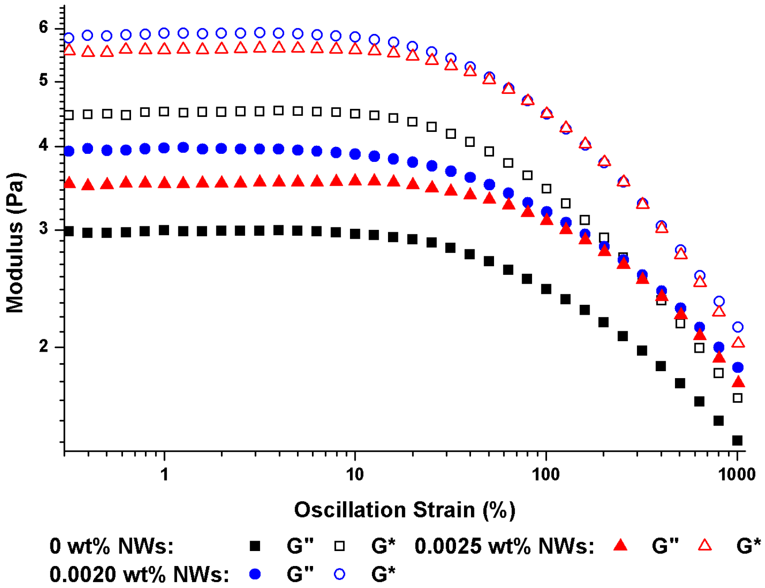


Figure S13: Loss (G") and complex ($|G^*|=[G'^2+G''^2]^{1/2}$) moduli from amplitude dependent oscillatory rheology of the solution of 0.5 wt% HEC-Np, 0.05 wt% PVA-MV with different concentration of $CePO_4$ NWs.

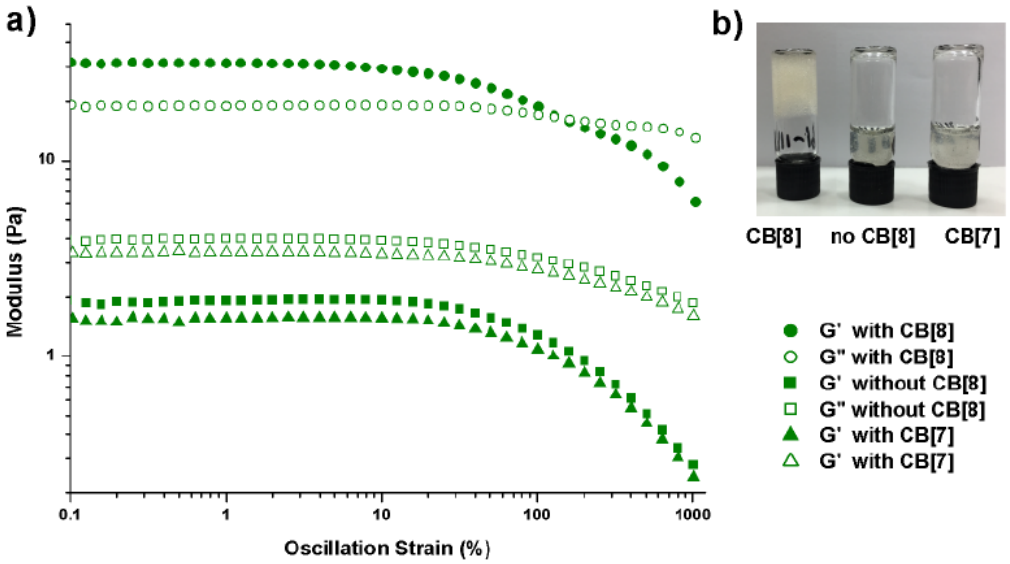


Figure S14: Storage (G') and loss (G") moduli from amplitude dependent oscillatory rheology for the control experiment. The gels was composed of 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.0020 wt% $CePO_4$ nanowire with CB[8], without CB[8] and with CB[7].

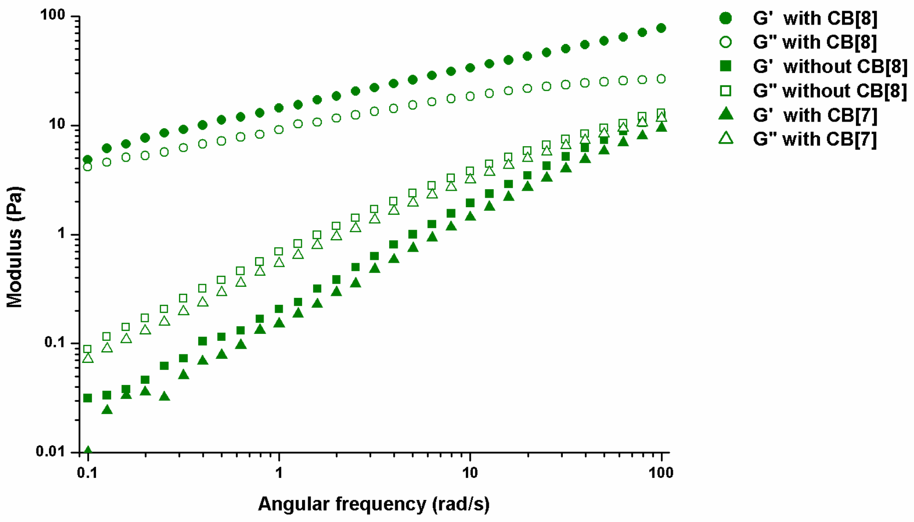


Figure S15: Storage (G') and loss (G") moduli from frequency dependent oscillatory rheology for the control experiment. The gels was composed of 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.0020 wt% $CePO_4$ nanowire with CB[8], without CB[8] and with CB[7].

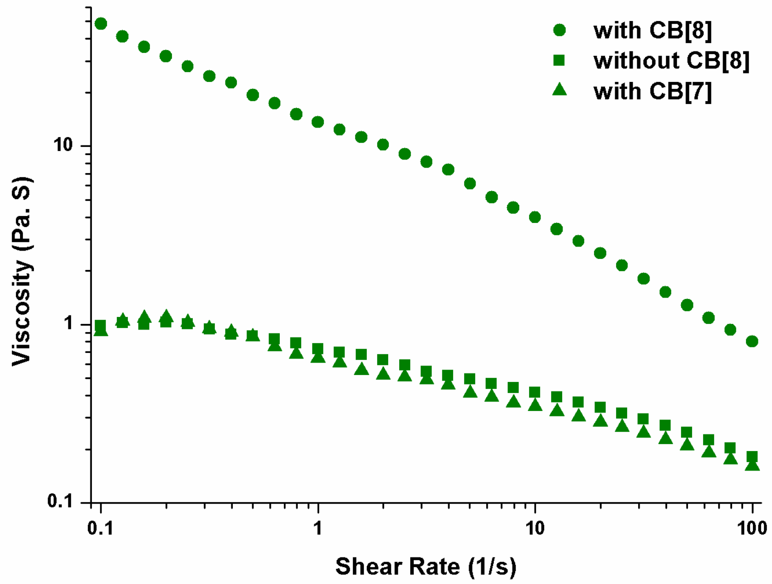


Figure S16: Shear dependent rheology for the control experiment. The gels was composed of 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.0020 wt% $CePO_4$ nanowire with CB[8], without CB[8] and with CB[7].

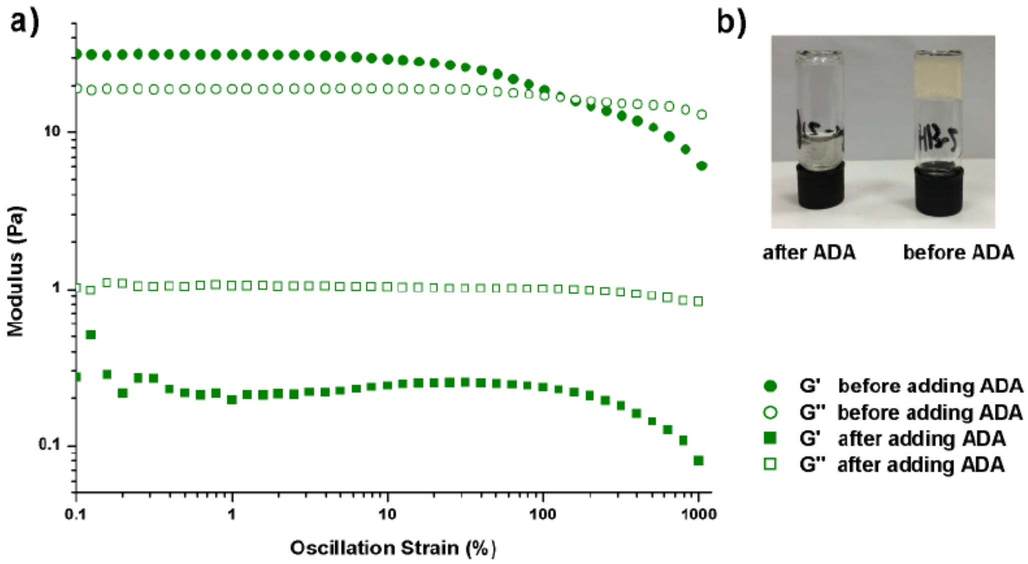


Figure S17: Storage (G') and loss (G") moduli from amplitude dependent oscillatory rheology for the control experiment. The gels was composed of 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.0020 wt% $CePO_4$ nanowire before and after adding competitive guest 1-adamantylamine (ADA).

S.7 Support Information

S.7.1 Materials and general methods

All starting chemicals were purchased from Sigma Aldrich and used as received unless stated otherwise. Poly(vinyl alcohol)(PVA, M_n = 205 KDa) first dissolved in water at 5 wt%, then precipitated from a solution of acetone and methanol (1:1) and dried overnight at 60 °C. Hydroxyethyl cellulose (HEC), with a number-average molecular weight (M_n) of 1.3 MDa, dried overnight in a vacuum oven at 105 °C before use. CB[7], CB[8][1,2] and MV-NCO[3] were prepared according to previously published protocols.

^{1}H NMR (500 MHz) spectra were recorded using Bruker Avance QNP 500 Cryo Ultrashield. Chemical shifts were measured in ppm (δ) in D2O with the internal reference set to δ 4.79 ppm.

Rheological characterisation was performed using a TA Instruments Discovery Hybrid Rheometer (DHR)-2 controlled stress rheometer fitted with a Peltier Plate set to 20 °C. All measurements were performed using a 40 mm parallel plate geometry (500 μm gap size) and analysed using TA Instruments TRIOS software. Dynamic oscillatory strain amplitude sweep measurements were conducted at a frequency of 10 rad/s between 0.1 % and 1000 % oscillation strain. Dynamic oscillatory frequency sweep measurements were performed at a 1% strain amplitude, between 0.01 to 100 rad/s. And the flow sweep tests were conducted between 0.01 and 100 S^{-1}.

ATR FT-IR spectroscopy was conducted using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory.

Transmission electron microscopy (TEM) characterisation was carried out on a FEI Philips Tecnai 20 TEM under an accelerating voltage of 80 kV. Samples were prepared by applying one drop of the as-synthesized microspheres onto a Holey R carbon coated copper TEM grid (400 mesh) and dried overnight.

Scanning electron microscopy (SEM) images were obtained using a Zeiss (Jena, Germany) FE-SEM with variable pressure at 1.5 keV. SEM samples were prepared by freezing of the supramolecular hydrogels in liquid nitrogen followed by lyophilization. The resulting materials were imaged after sputtering.

S.7.2 Synthesis of PVA-MV

Poly(vinyl alcohol)(PVA, 1.00 g, 205 KDa, M_n) and MV-NCO were first dissolved in NMP (60 mL). After addition of dibutyltin dilaurate (3 drops), the mixture was stirred overnight at room temperature. Then the mixture was dialysis against NaCl solution (0.1 M, 24 h) and water (48 h) to exchange counter-ion before freeze drying to yield a yellowish solid (1.56 g, 96 %). ^{1}H NMR (500 MHz, D_2O)δ(ppm=) 9.17-8.96 (br, MV aryl-*H*), 8.52-8.42 (br, MV aryl-*H*), 4.56-4.51 (br, MV-CH_2), 4.42 (s, MV-CH_3), 4.00-3.89 (br, MV-CH_2-CH_2-OCN- and -NCO-C*H* from the backbone), 2.95-2.83 (br, -C*H*2-NCO), 2.05-1.25 (br, polymer backbone and hexamethylene linker).

S.7.3 Synthesis of HEC-Np

HEC-Np was synthesised according to previous literature.[4]

Hydroxyethyl cellulose (HEC, 2.00 g, 1.3 MDa, M_n) was dissolved in *N*-methylpyrrolidone (NMP, 300 ml). The mixture was heated to 110 °C under nitrogen to yield a pale yellow clear solution. The solution was cooled to room temperature and Np-NCO (60.2 mg, 3.55 mmol) as well as dibutyltin dilaurate (6 drops) was added. After stirring overnight, the solution was precipitated from cooled acetone. The solid was collected by filtration. Next it was dissolved in DI H_2O before dialysis against H_2O for three days. After freeze drying, the product was obtained as white solid (2.02 g, 98 %). ^1H NMR (500 MHz, D_2O)δ(ppm=) 7.91-7.35 (m, nathphyl), 4.28-2.93 (br, polymer backbone).

S.7.4 Preparation of $CePO_4$ nanowire

The $CePO_4$ nanowires were prepared using a hydrothermal method. In the synthesis, $Ce(NO_3)_3$ (0.40 g) and Na_3PO_4 (0.30 g) were dissolved in 30 mL of DI water in a Teflon autoclave reactor, the pH of the solution adjusted to 2 using HCl (aq, 1M). After being sealed the solution was heated at 170 °C for 10 h in an electric oven, which yielded a clear colloid. The products were then separated by centrifugation at 10,000 rpm and washed with DI water.

The phase of the products was characterised via powder X-ray diffraction (XRD) on Bruker D8 Advance with the energy of 40 kV and 40 mA. Their morphology was verified using Transmission electron microscopy (TEM) on a FEI Tecnai F20 operated at 200 kV.

S.7.5 Hydrogel preparation, example procedure

An example of the general hydrogel preparation is described here for a HEC-Np/PVA-MV/CB[8]/nanowire 0.5/0.05/0.05/0.001 wt% gel. Firstly, HEC-Np (7.5 mg) was dissolved in DI water (0.5 mL) with stirring and mild heating. Secondly, a mixture of PVA-MV (0.75 mg) and CB[8] (0.75 mg) was dissolved in water (0.5 mL) and sonicated <5 min). Similarly $CePO_4$ nanowires (0.015 mg) were first dispersed in DI water (0.5 mL) and sonicated. Finally, the solutions were mixed and vortexed for approximately 1 s to achieve a combined hydrogel and any bubbles were removed by centrifuge at 10000 rpm for 3 minutes.

References

[1] D. Z. Jiao, N. Zhao and O. A. Scherman, *Chem. Commun.*, 2010, **46**, 2007–2009.

[2] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540–541.

[3] F. Biedermann, E. A. Appel, J. del Barrio, T. Gruendling, C. Barner-Kowollik and O. A. Scherman, *Macromolecules*, 2011, **44**, 4828–4835.

[4] E. A. Appel, X. J. Loh, S. T. Jones, F. Biedermann, C. A. Dreiss and O. A. Scherman, **134**, 11767–11773.