Supporting Information

Multi-stimuli-responsive induced circular dichroism of polyoxometalates in natural polysaccharide hydrogels

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Experimental Section

Agarose (molecular biology grade) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. κ-/ι- carrageenan and sodium ascorbate (SA) were purchased from J&K Scientific Ltd. Commercially available Keggin POMs {H₄[SiO₄MO₁₂O₃6]} (SiMo₁₂), H₃PMO₁₂O₄₀ (PMo₁₂), H₄[SiW₁₂O₄₀] (SiW₁₂), H₂O₄₀PW₁₂ (PW₁₂)}, were purchased from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water was used to prepare all aqueous solutions from a Millipore Milli-Q system. Potassium chloride and 30% H₂O₂ solution were purchased from Beijing Chemical Works. All the reagent was used as received. K₆P₂W₁₈O₆₂ (P₂W₁₈) and (NH₄)₆[P₂Mo₁₈O₆₂]·12H₂O (P₂Mo₁₈) were synthesized according to the published procedures.¹²

Characterization.

Absorption spectra were recorded on a Lambda 35 UV-Vis spectrometer. CD spectra were recorded on a Jasco J-810 circular dichroism spectrometer, and a circular quartz cell with a length of 2 mm or 0.2 mm was used for characterization. TEM images were recorded from a JEOL JEM-2100 (Japan) transmission electron microscopy operated at 200kV. Isothermal titration calorimetry experiment was taken in a MicroCal Itc200 apparatus at 25 °C. The POM aqueous solution (0.5689 mM) were titrated into a agarose, κ-carrageenan, ι-carrageenan aqueous solutions (1.5mM) via a 280 μL syringe, respectively. The total injection was 29 drops.

Preparation of agarose hydrogel hybrids.

In a typical experiment, 60 mg agarose powder was added to 3mL ultrapure water at 100 °C and stirred vigorously 5 min. A certain amount of POMs was added to the above homogeneous solution and then cool down to room temperature to form hydrogel hybrid. (Agarose: c = 20 mg mL⁻¹; PMo₁₂: c = 5 mg mL⁻¹; SiMo₁₂: c = 5 mg mL⁻¹; P₂Mo₁₈: c = 1.5 mg mL⁻¹)

Preparation of carrageenan hydrogel hybrids.

The procedure was similar to the agarose ones. 5 mg/ml κ- carrageenan and 15 mg/ml ι- carrageenan were prepared at 90°C, and 150 mM KCl solution was added to hot solution to promote the conformational transition from random coil to helix. (ι-carrageenan: c = 15 mg mL⁻¹; κ-carrageenan: c = 5 mg mL⁻¹; KCl: c = 150mM; PMo₁₂: c = 5 mg mL⁻¹; SiMo₁₂: c = 5 mg mL⁻¹; P₂Mo₁₈: c = 1.5 mg mL⁻¹; PW₁₂: c = 3 mg mL⁻¹; SiW₁₂: c = 3 mg mL⁻¹; P₂W₁₈: c = 1.5 mg mL⁻¹)
For the control hydrogel hybrids, no POMs was added.

**Preparation of hydrogel hybrids tunning by external conditions.**

We selected κ-carrageenan hydrogel hybrids as an example. \( \kappa \)-carrageenan: \( c = 5 \text{ mg mL}^{-1} \); KCl: \( c = 150\text{mM} \); SiMo\(_{12}\): \( c = 3 \text{ mg mL}^{-1} \)

**Supplementary Figures and Tables**

**Fig. S1** Isothermal titration calorimetry data of the addition of the P\(_2\)Mo\(_{18}\) aqueous solution into the agarose (a), ι-carrageenan (b), κ-carrageenan (c) aqueous solutions at 25°C.

**Fig. S4S2** UV–Vis spectra and CD spectra of pure polyoxotungstates and agarose.
**Fig. S3** The reversible CD spectra of SiMo\(_{12}\)/κ- carrageenan hybrids at different temperature between 15°C and 75°C.

**Fig. S4** CD spectra of SiMo\(_{12}\)/κ- carrageenan hybrids with different concentration of SiMo\(_{12}\) (a), κ-carrageenan (b).

**References**