

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 { $\text{H}_4[\text{SiO}_4\text{MO}_{12}\text{O}_{36}]$ (SiMo_{12}), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}), $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ (SiW_{12}), $\text{H}_3\text{O}_{40}\text{PW}_{12}$ (PW_{12})}, 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% H_2O_2 solution were purchased from Beijing Chemical Works. All the reagent was used as received. $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (P_2W_{18}) and $(\text{NH}_4)_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 12\text{H}_2\text{O}$ (P_2Mo_{18}) were synthesized according to the published procedures.^{1,2}

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, ι -carrageenan, κ -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: $c = 20 \text{ mg mL}^{-1}$; PMo_{12} : $c = 5 \text{ mg mL}^{-1}$; SiMo_{12} : $c = 5 \text{ mg mL}^{-1}$; P_2Mo_{18} : $c = 1.5 \text{ mg mL}^{-1}$)

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: $c = 15 \text{ mg mL}^{-1}$; κ -carrageenan: $c = 5 \text{ mg mL}^{-1}$; KCl: $c = 150\text{mM}$; PMo_{12} : $c = 5 \text{ mg mL}^{-1}$; SiMo_{12} : $c = 5 \text{ mg mL}^{-1}$; P_2Mo_{18} : $c = 1.5 \text{ mg mL}^{-1}$; PW_{12} : $c = 3 \text{ mg mL}^{-1}$; SiW_{12} : $c = 3 \text{ mg mL}^{-1}$; P_2W_{18} : $c = 1.5 \text{ mg mL}^{-1}$)

For the control hydrogel hybrids, no POMs was added.

Preparation of hydrogel hybrids tuning by external conditions.

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

Supplementary Figures and Tables

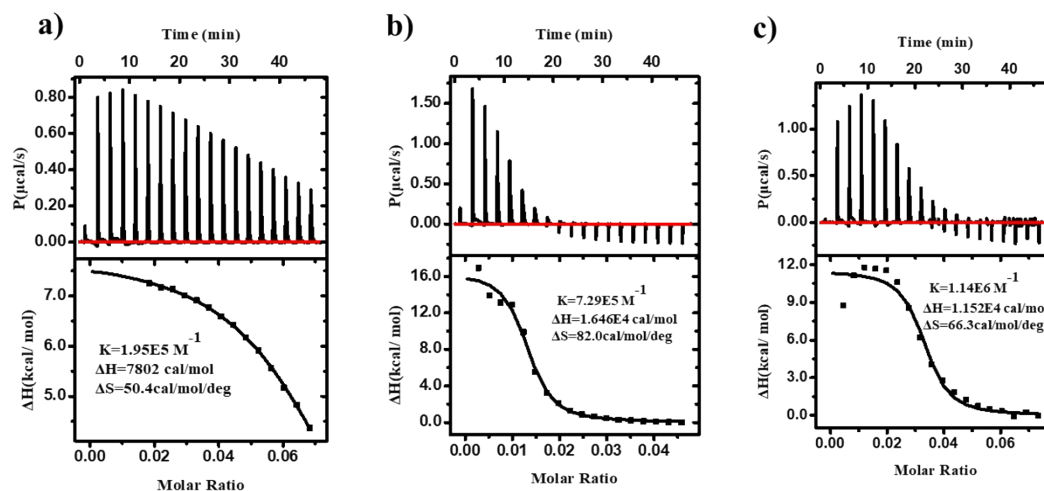


Fig. S1 Isothermal titration calorimetry data of the addition of the P_2Mo_{18} aqueous solution into the agarose (a), ι -carrageenan (b), κ -carrageenan (c) aqueous solutions at 25°C .

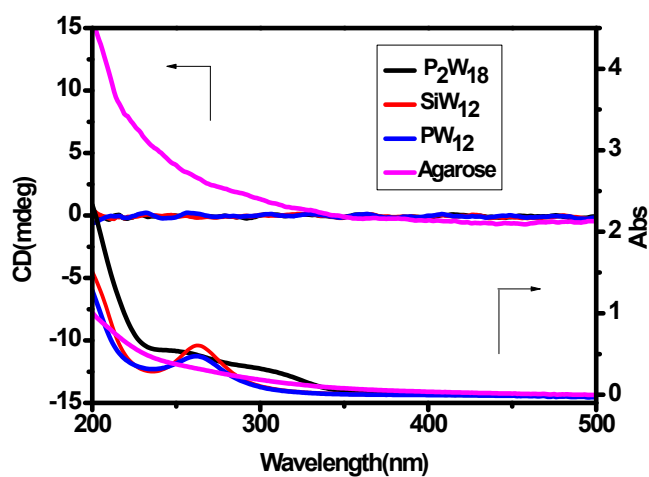


Fig. S1S2 UV-Vis spectra and CD spectra of pure polyoxotungstates and agarose.

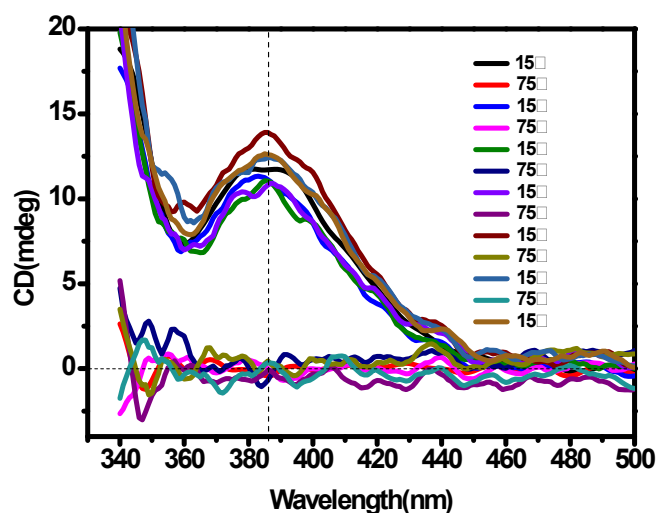


Fig. S3 The reversible CD spectra of SiMo₁₂/κ-carrageenan hybrids at different temperature between 15°C and 75°C.

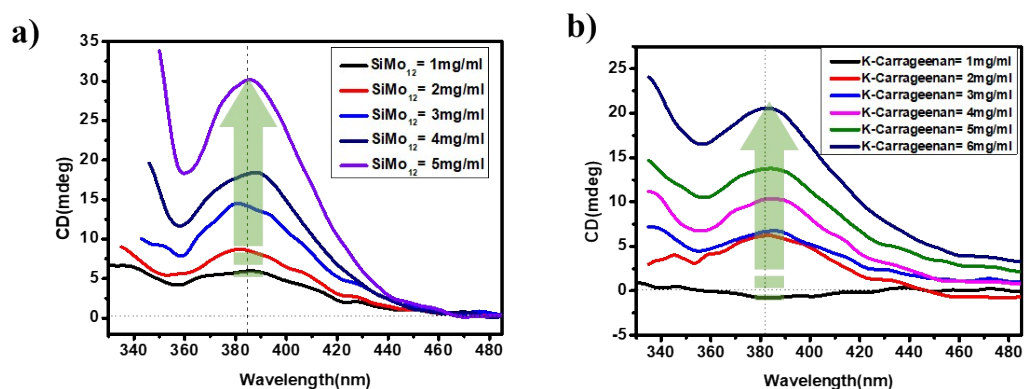


Fig. S4 CD spectra of SiMo₁₂/κ-carrageenan hybrids with different concentration of SiMo₁₂ (a), κ-carrageenan (b).

References

- 1 L. E. Briand, G. M. Valle and H. J. Thomas, *J. Mater. Chem.*, 2002, **12**, 299.
- 2 C. R. Graham and R. G. Finke, *Inorg. Chem.*, 2008, **47**, 3679.