Supplementary Information (SI) for Soft Matter.
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Supplementary Information

Cluster-Directed Ionic Framework Supramolecular Hydrogel with High Temperature Tolerability and Enhanced Water Evaporation

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S1. Materials

The general chemicals, p-Toluidine, phenol, triethylene glycol (TrEG), and p-toluenesulfonyl chloride were purchased from Sinopharm Group Chemical Reagent Co., Ltd. DMF was stirred with CaH_2 for 7 days and then distilled under reduced pressure to remove water. Acetonitrile was dried by refluxing with P_2O_5 for 6 hours and then distilled to remove water. Other chemicals were used as received without further treatment. Doubly distilled water was used throughout the experiments.

S2. Measurements

Scanning electronic microscopic (SEM) measurement was performed on a JEOL JSM-6700F field emission scanning electron microscope. X-ray diffraction (XRD) data were recorded on a Rigaku SmartLab 3 X-ray diffractometer using Cu Kα1 radiation at wavelength of 1.542 Å. Transmission electronic microscopic (TEM) images were obtained on a field emission electron microscope (JEOL JEM-2100F) with accelerating voltage of 200 KV without staining. Rheology measurements were executed on a Discovery Hybrid Rheometer (TA HR-1, USA). DSC was carried out on a TA DSCQ20 instrument at a scanning rate of 10 °C min-1 ranging from 40 °C to 160 °C.

S3. Preparation of CPR·2Br Supramolecular Complex

First, weigh 10 mg of DCG·2Br (0.012 mmol) and 22.7 mg of α-CD (0.024 mmol), dissolve them in 300 μL of water, and stir for 12 hours. The resulting supramolecular complex, CPR·2Br, with positive charges at both ends, is left standing for further use.[1]

S4. Preparation of the ISF Hydrogels

$AlMo_6^{3-}$ ISF Hydrogel: Weigh 91.0 mg of $Na_3(H_2O)_6[Al(OH)_6Mo_6O_{18}]$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

PWV^{4-} ISF Hydrogel: Weigh 135.4 mg of $K_4PW_{11}VO_{40}$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

$SiWV^{5-}$ ISF Hydrogel: Weigh 137.1 mg of $K_5SiW_{11}VO_{40}$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

CoW^{6-} ISF Hydrogel: Weigh 122.2 mg of $K_6CoW_{12}O_{40}$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

PW_{11}^{7-} ISF Hydrogel: Weigh 98.4 mg of $K_7PW_{11}O_{39}$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

SiW_{11}^{8-} ISF Hydrogel: Weigh 87.2 mg of $K_8SiW_{11}O_{39}$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

BW_{11}^{9-} ISF Hydrogel: Weigh 78.4 mg of $K_8H[BW_{11}VO_{39}]$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

$ZnWMn_2^{12-}$ ISF Hydrogel: Weigh 100.4 mg of $Na_{12}[ZnWMn_2(ZnW_9O_{34})_2]$, dissolve it in 1 mL of water, and add 0.1 mL of POM aqueous solution to the pre-prepared CPR·2Br aqueous solution. The mixture is then shaken and mixed evenly to obtain the supramolecular hydrogel.

S5. Characterizations of ISF Hydrogels.

Table S1. The ICP and organic elemental analysis of ISF assembly of $CPR^{2+}/AlMo_6^{3-}$ at the molar ratio of 3:2.

$[C_{42}H_{42}N_6O_4\ (C_{36}H_{60}O_{30})_2]_{1.5}(AlMo_6H_6O_{24})(NaBr)_3(H_2O)_5$						
%	N	C	H	Na	Al	Mo
Found	2.66	38.31	4.89	1.13	0.78	10.65
Calculate	2.36	38.37	4.87	1.28	0.50	10.75

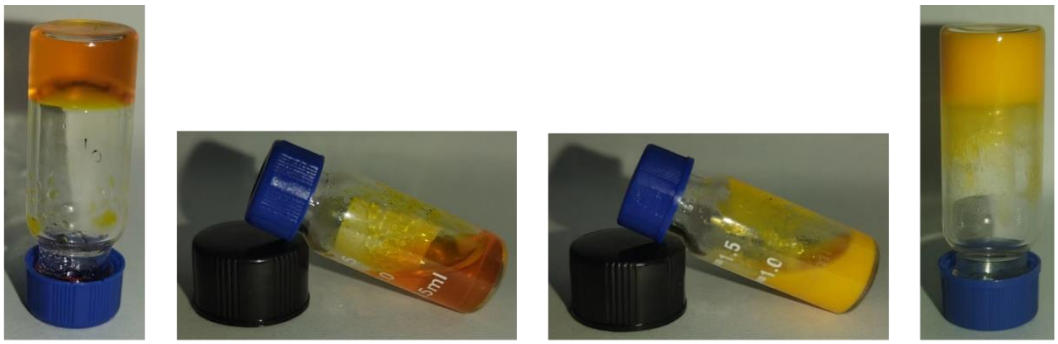


Fig. S1. Photographs of DCG·2Br hydrogel, CPR·2Br aqueous solution, DCG·2Br/$Na_3[AlMo_6]$ jelly state, and CPR^{2+}–$AlMo_6^{3-}$ ISF hydrogel.

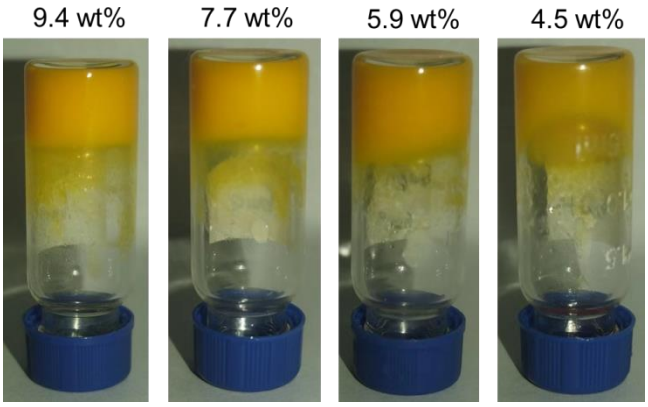
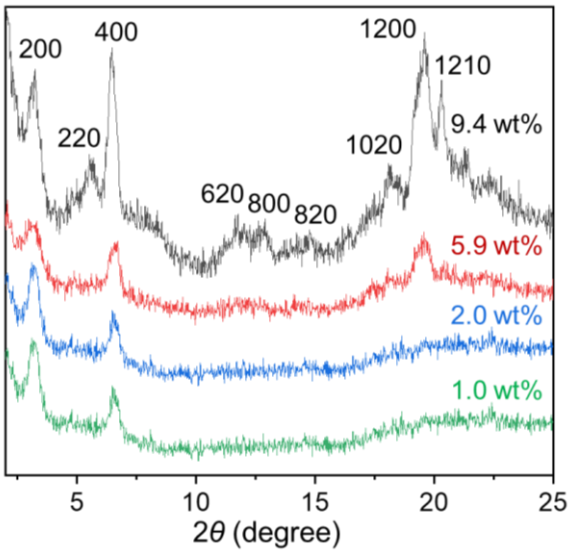


Fig. S2. Photographs of the ISF hydrogels with different concentrations at room temperature.



2θ/°	d/nm	hkl	Error/nm
3.2	2.75	200	0.02
5.5	1.60	220	0
6.5	1.36	400	0.02
11.7	0.75	620	0.01
12.8	0.69	800	0
14.7	0.60	820	0
18.1	0.49	1020	0
19.5	0.45	1200	0.01
20.3	0.44	1210	0

Fig. S3. XRD patterns of the ISF xerogels prepared via freeze-drying at different concentrations (1.0, 2.0, 5.9 and 9.4 wt%).

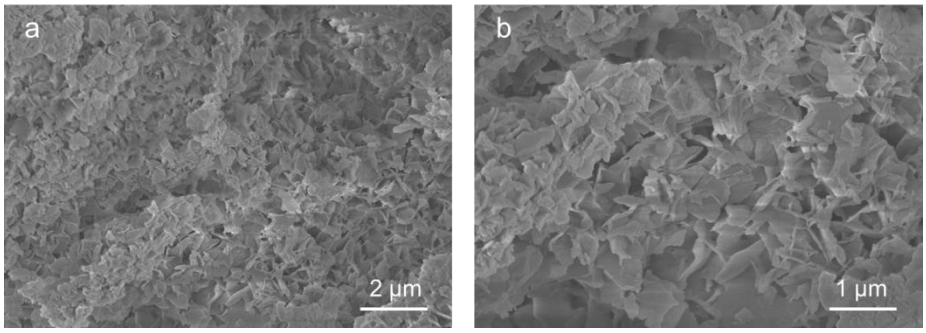


Fig. S4. (a) SEM image and (b) local magnification of ISF xerogel (9.4 wt%) prepared by freeze-drying.

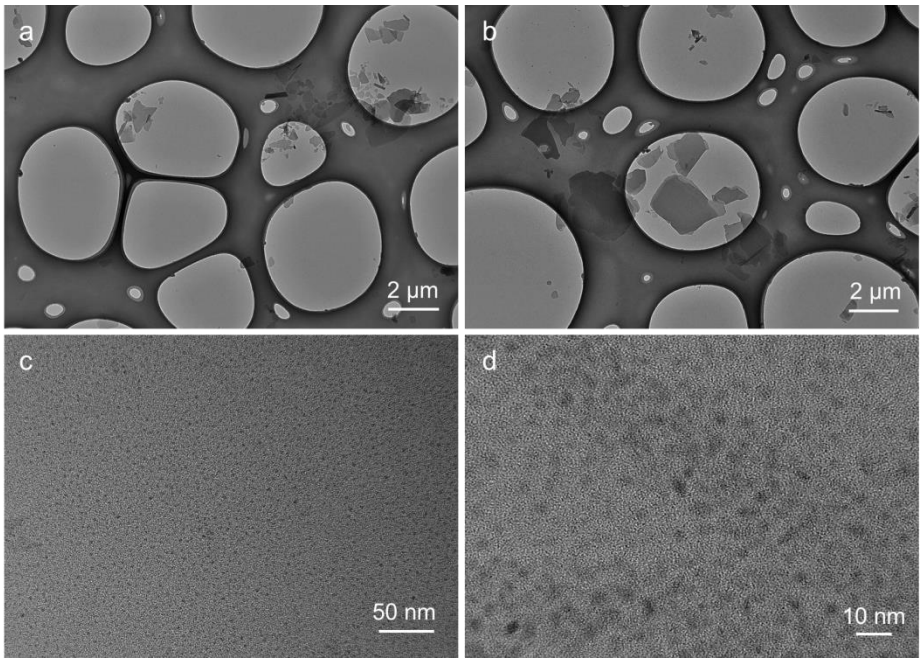


Fig. S5. (a, b) TEM images and (c, d) its local magnification of ISF xerogel (9.4 wt%) prepared by freeze-drying.

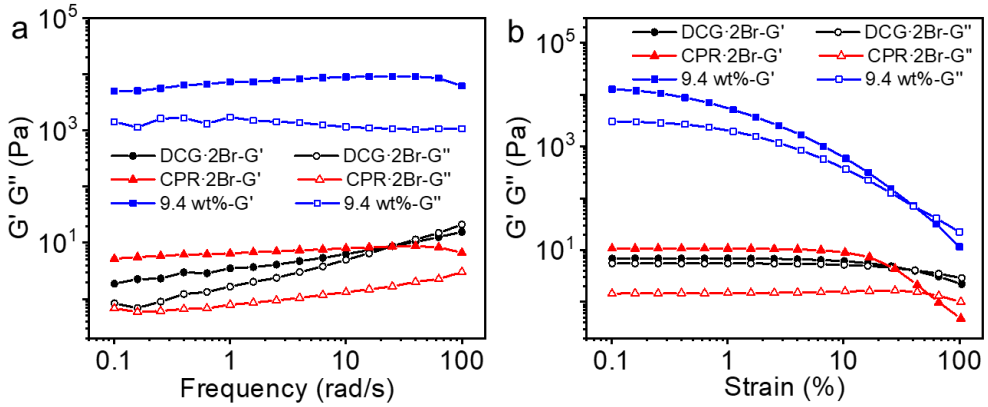


Fig. S6. (a, b) Rheology versus angular frequency sweeps and analysis of the DCG·2Br,

CPR·2Br, and the CPR–$AlMo_6$ ISF hydrogel (9.4 wt%).

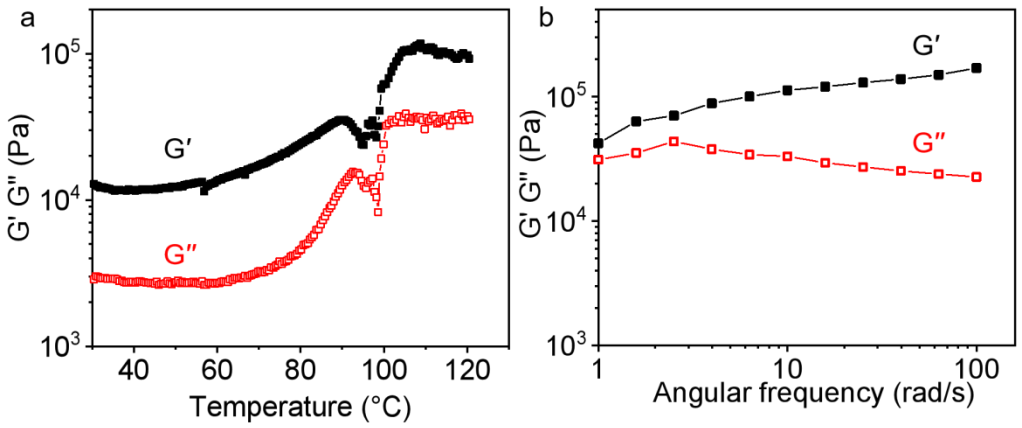


Fig. S7. (a) Rheology of the prepared ISF hydrogel versus temperature from 30 °C to 120 °C and (b) angular frequency sweeps at 120 °C

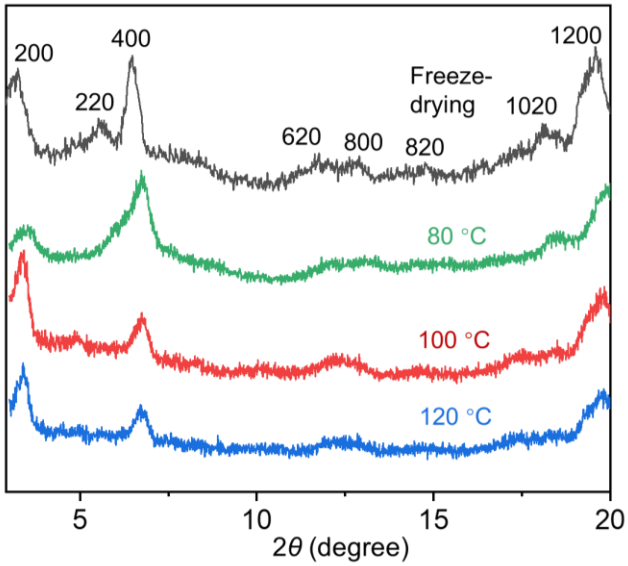


Fig. S8. XRD patterns of the ISF xerogels after freeze-drying and drying at different temperature (room temperature, 80, 100 and 120°C).

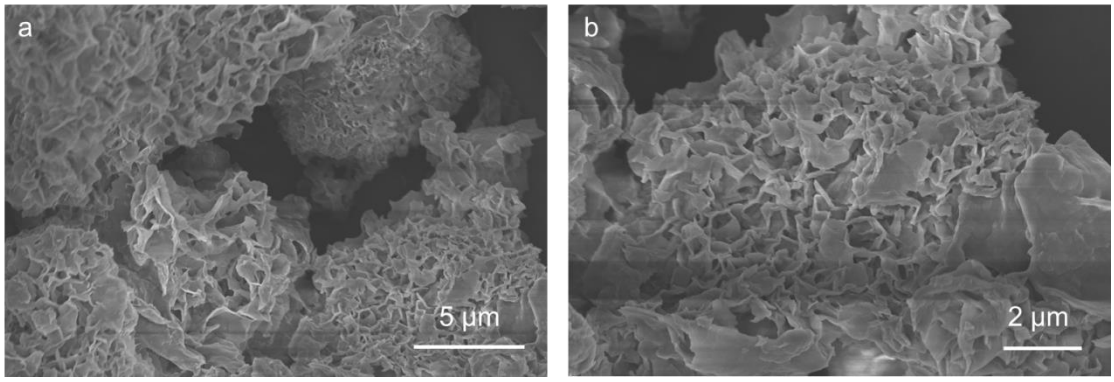


Fig. S9. (a, b) SEM images of ISF xerogel (9.4 wt%) prepared by heating to dry at 80 °C.

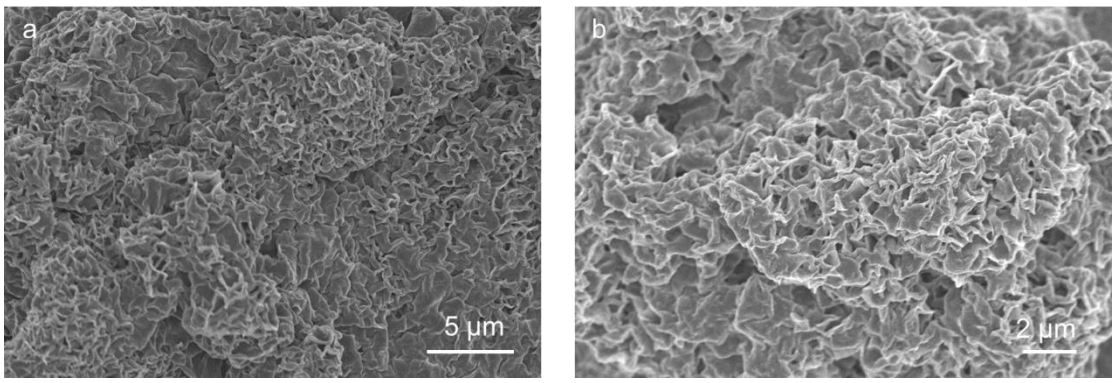


Fig. S10. (a, b) SEM images of ISF xerogel (9.4 wt%) after drying at 100 °C with different magnification scales.

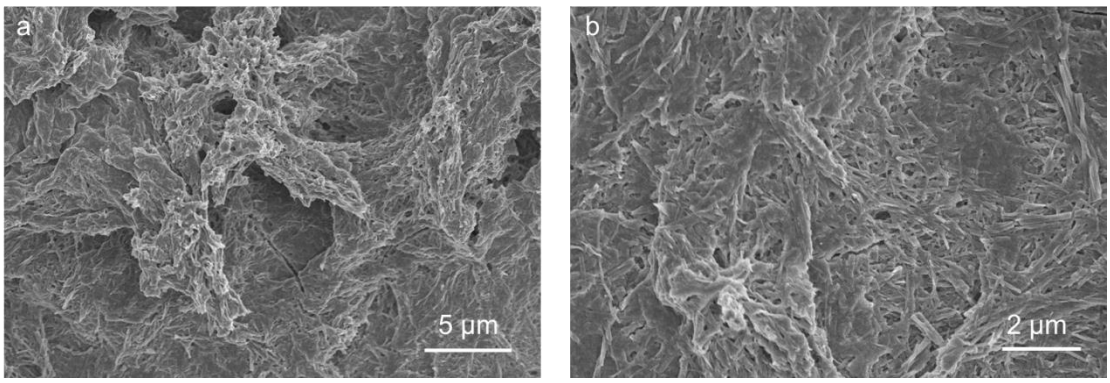


Fig. S11. (a, b) SEM images of ISF xerogel (9.4 wt%) after drying at 120 °C with different magnification scales.

Table S2. The summary of the gel-sol transition temperature (T) of the hydrogels prepared at 1:1 charge ratio of CPR·2Br and the used POMs.

POM	$AlMo_6^{3-}$	PWV^{4-}	$SiWV^{5-}$	CoW^{6-}	PW_{11}^{7-}	SiW_{11}^{8-}	BW_{11}^{9-}	$ZnWMn_2^{12-}$
T/°C	>110	78	76	76	74	72	72	72

Fig. S12. Photographs of the gel-sol phase transition of the hydrogel prepared by PWV^{4-} and CPR^{2+} upon heating and then cooling.

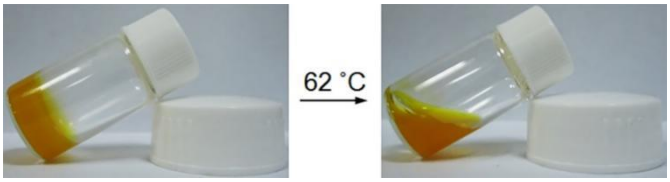


Fig. S13. Photographs of the phase transition from gel to sol of the hydrogel formed by CPR^{2+} and phosphate PO_4^{3-} at 1:1 of charge ratio upon heating.

Table S3. The summary of the gel-sol transition temperature (T) of the hydrogel prepared at 3:2 molar ratio of CPR·2Br and POMs.

POM	$AlMo_6^{3-}$	CoW^{6-}	$ZnWMn_2^{12-}$
T/°C	>110	96	88

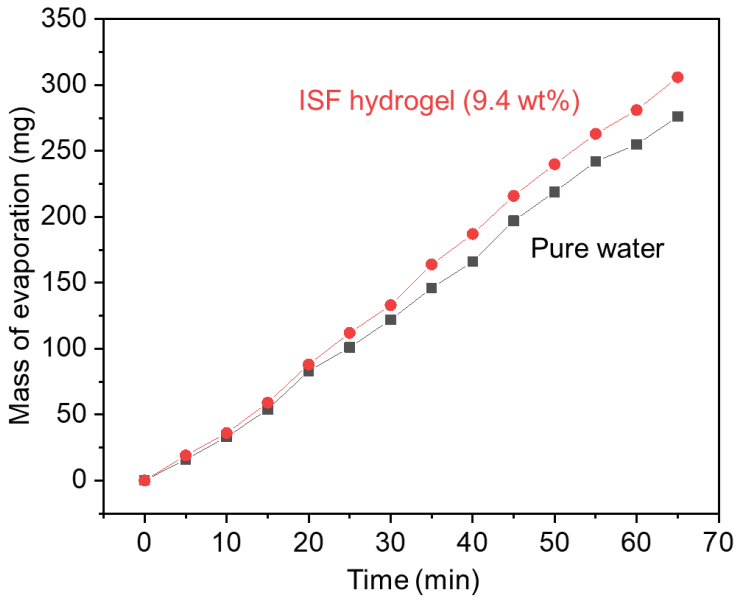


Fig. S14. Evaporation rate of pure water and ISF hydrogel (9.4 wt%) versus the time at the temperature of 80°C.

S6. Reference

[1] L. Yue, S. Wang, D. Zhou, H. Zhang, B. Li, L. X. Wu, *Nat. Commun.*, 2016, **7**, 10742