Supporting Information

Temperature- and Salt-Responsive Polyoxometalate-Poly(N-isopropylacrylamide) Hybrid Macromoleules in the Aqueous Solution

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Materials and sample preparation.
Sodium phosphotungstate (Sigma-Aldrich), poly(N-isopropylacrylamide) triethoxysilane terminated (PNIPAM, Sigma-Aldrich), sodium carbonate (Na_2CO_3, Sigma-Aldrich), potassium chloride (KCl, Sigma-Aldrich), hydrochloric acid (HCl, Fisher Scientific), tetrabutylammonium chloride (TBA, Sigma-Aldrich) and acetonitrile (Sigma-Aldrich) were all used as received.

For a typical light scattering measurement, the sample was dissolved in deionized (DI) water. The obtained solutions were filtered with 200 nm pore-size hydrophilic polytetrafluoroethylene (PTFE) membrane filters and put into dust-free light-scattering sample vials. Salt solution was also filtered and added to the aqueous solution.

Instrumentation and Characterization.
Size Exclusion Chromatography (SEC). SEC analyses were performed using a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with refractive index (RI) detector. SEC used two separation columns of SuperAW3000 and SuperAW-H (TSK-GEL, Tosoh). *N,N*-Dimethylformamide (DMF) (with 0.01 M LiBr) was used as the eluent with a flow rate of 0.8 mL/min at 50 °C. The molecular mass was calculated from universal calibration based on poly(methyl methacrylate) standards.

Nuclear Magnetic Resonance (NMR) Spectroscopy. The ^{1}H and ^{31}P NMR spectra of the products were obtained in D_2O (99.8% D, Sigma-Aldrich) or acetonitrile-d_3 (99.9 % D, Sigma-Aldrich) using a Varian NMRS 500 spectrometer equipped with an auto-sampling robot at 30 °C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet. Data analysis was done by ACD/NMR Processor Software. The ^{1}H NMR spectra were referenced to the residual proton impurities in D_2O δ 4.80 ppm or in CD_3CN at 1.95 ppm.

Fourier-transform Infrared (FTIR) Spectroscopy. FTIR spectra were recorded on a Shimadzu MIRacle 10 ATR-FTIR spectrometer from 600 to 4000 cm^{-1}. Resolution was 4 cm^{-1} and scan numbers were 128. Data analysis was done by Win-IP Pro Software.

Matrix-assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectroscopy. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics) equipped with a Nd:YAG laser emitting at 355 nm. The matrix compound used here was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 99%, Aldrich) and was dissolved in $CHCl_3$ at a concentration of 20.0 mg/mL. When necessary, sodium trifluoroacetate (NaTFA) was used as the cationizing agent and was prepared as a MeOH/$CHCl_3$ (v/v = 1/3) solution at a concentration of 10.0 mg/mL. The matrix and cationizing agent solutions were mixed in the ratio of 10/1 (v/v). The sample was prepared by depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample. Mass spectra were measured in the reflection mode, and the mass scale was calibrated externally with a PMMA or PS standard at the molecular weight region under consideration. Data analyses were conducted with the Bruker's flexAnalysis software.

Static Light Scattering (SLS). A commercial Brookhaven LLS spectrometer equipped with a solid-state laser operating at 532 nm was used for both SLS and DLS measurements. SLS experiments were performed at scattering angles between 40 and 120° at 2° intervals. The Rayleigh–Gans–Debye equation[1] could be used to obtain the weight-average molar mass (M_w) and the radius of gyration (R_g) of the assemblies.

Dynamic Light Scattering (DLS). DLS measured the intensity–intensity time correlation function with a BI-9000AT multichannel digital correlator. The field correlation function $|g^{(1)}(\tau)|$ was analyzed by the CONTIN method[2] to yield the distribution of the characteristic line width Γ from $|g^{(1)}(\tau)| = \int G(\Gamma)e^{-\Gamma\tau}d\Gamma$. The normalized distribution function of the characteristic line width $G(\Gamma)$ can be used to determine the apparent translational diffusion coefficient, $D_{app} = \Gamma/q^2$. The hydrodynamic radius R_h is related to D by means of the Stokes–Einstein equation, $R_h = kT/6\pi\eta D$, in which k is the Boltzmann constant and η is the viscosity of the solvent at temperature T. DLS measurements led to the particle-size distribution in solution from a plot of $\Gamma G(\Gamma)$ versus R_h. The R_h of the particles was obtained by extrapolating Rh,app to zero scattering angle.

Transmission Electron Microscopy (TEM). Bright-field TEM was carried out with a JEOL-1230 electron microscope with an accelerating voltage of 120 kV, and the images were taken with a digital CCD camera and processed with the digital imaging system accessory. Samples for the TEM analysis were prepared by dripping 10 μL of the solution samples onto the carbon-film-coated copper grids. The excess amount of solution was wicked away by a piece of filter paper, and samples were then allowed to dry under ambient conditions.

Zeta Potential Analysis. Zeta potential analysis measurements were performed with a Malvern Instruments Inc. zeta potential analyzer equipped with a red laser operating at 633 nm wavelength and with an accuracy of ±2% for filtered samples. The sample chamber was kept at (25±0.1) °C, and all sample solutions were loaded 30 min prior to measurements to achieve thermal equilibrium with the chamber.

Synthesis of POM-PNIPAM hybrid.

1. Synthesis of $K_7[PW_{11}O_{39}]$ 1-vacant Keggin
The precusor $K_7[PW_{11}O_{39}]$ 1-vacant Keggin was systhesized according to previous literature.[3]

^{31}P NMR (500 MHz, D_2O): δ =-10.56 ppm.

2. Synthesis of POM-PNIPAM hybrid
To a suspension of $K_7[PW_{11}O_{39}]$ (1 eq.) in acetonitrile was added tetrabutylammonium chloride (TBA, 7.5 eq.). Then consecutively, poly(N-isopropylacrylamide) (2.2 eq.) and a 1M HCl solution (4.4 eq.) were added dropwise. After stirring overnight at room temperature, the solution was filtered and the solvent was evaporated. The solid residue was washed with DI water and dried in vacuum.

FTIR (cm^{-1}): 3615, 3543, 2975, 2944, 1645, 1539, 1445, 1376, 1109 (Si-O-Si), 967(W=O, as), 874(W-O$_a$-W, as), 827(W-O$_b$-W, as)

^{31}P NMR (500 MHz, Acetonitril-d$_3$): δ=-13.00 ppm.

^1H NMR (CD$_3$CN): δ= 3.96 (br, 1H, PNIPAM), 3.14 (t, 1H, TBA), 1.49-1.81(m&br, 2H in PNIPAM, 1H in TBA), 1.41 (m, 1H, TBA), 1.15 (s, 6H, PNIPAM), 1.01 (t, 1.5H, TBA).

MALDI-TOF (Acetonitrile): Take the example of 38 repeat units for calculation.
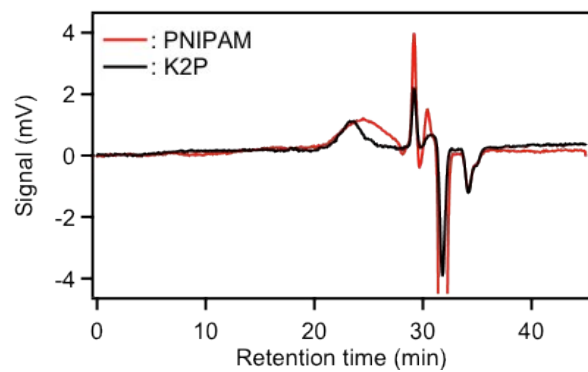Calculated $[M \cdot H^+_4]^+$ 7231.8 Da, found 7232.2 Da.

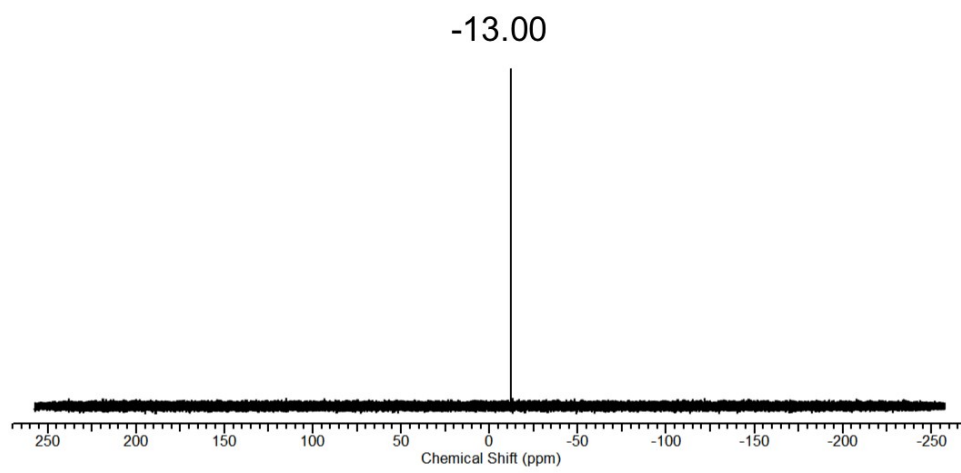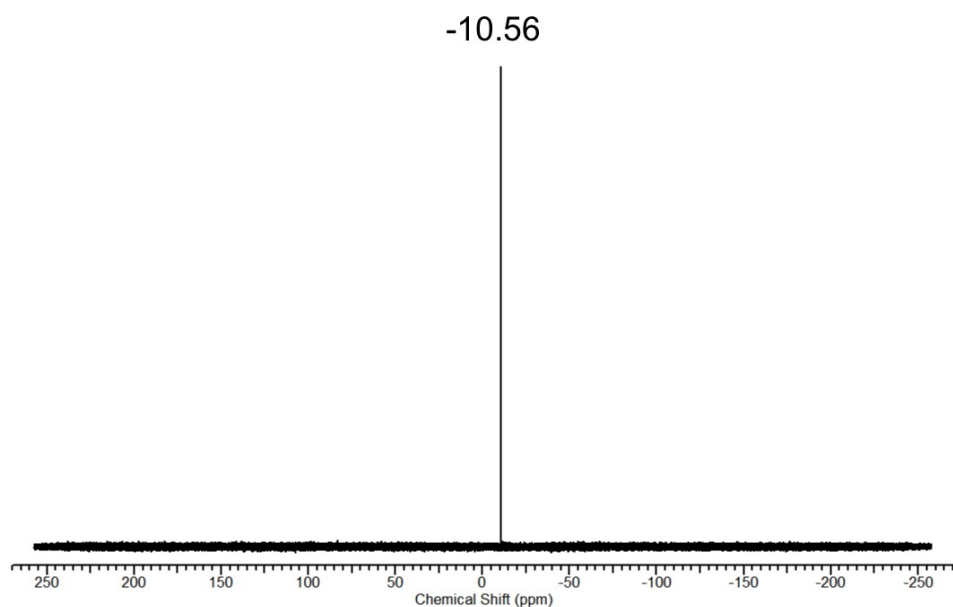**Figure S1.** The SEC measurements of the pure PNIPAM and the K2P hybrid.

-10.56

-13.00

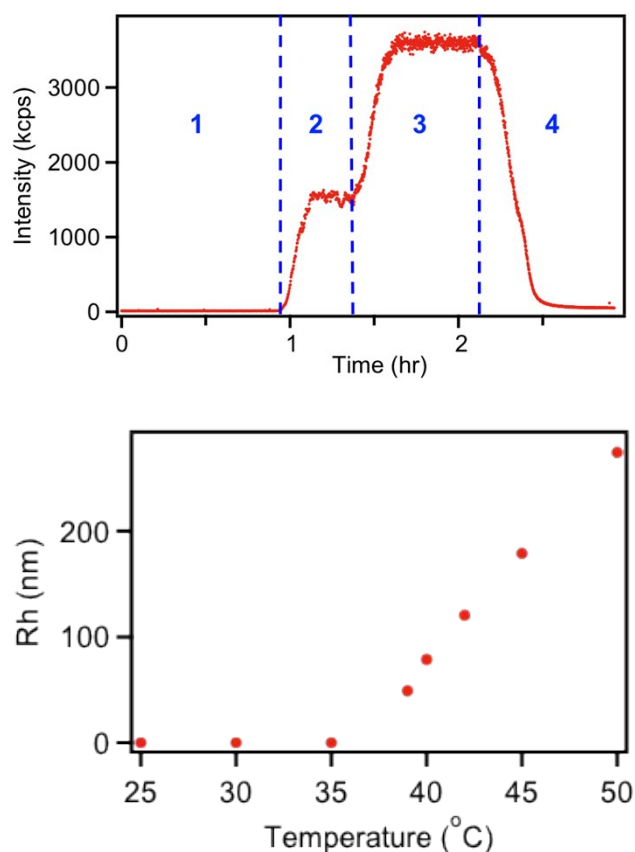**Figure S2.** ^{31}P NMRs of 1-vacant Keggin and POM-PNIPAM hybrid.

Figure S3. Top: Time-resolved SLS monitoring results of K2P (with K^+ ions as counterions) solution during varying the temperature which is divided into 4 regions (Regions: 1. Starting from room temperature RT, gradually increasing T to 35°C; 2. T is increase to 40°C; 3. T is increased to 45 °C; 4. T is decreased to 35 °C.). Bottom: Average R_h of the spherical structures formed by K2P-K as a function of temperature, measured by DLS.
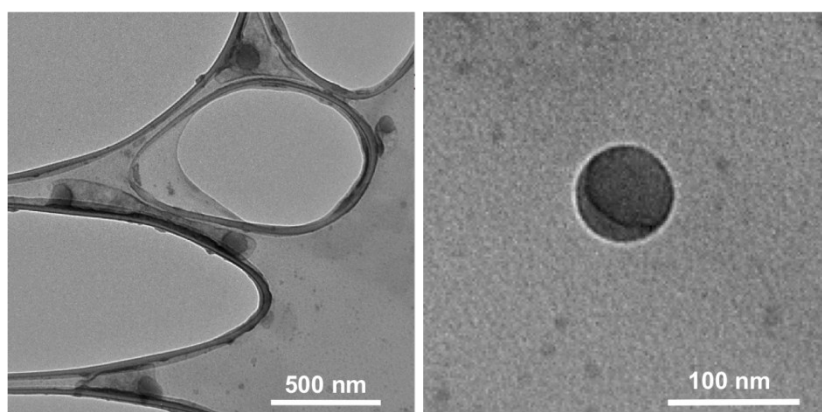

Figure S4. TEM images of the assemblies formed in 0.2 mg/mL K2P water solution at room temperature.

Table S1. Temperatures of triggering aggregation and aggregate sizes formed at 39 °C in PNIPAM solutions without and with adding different salts.

	No Salt	Na^+	Cs^+
Temperature (°C)	38	39	38
R_h (nm)	125	122	122

Reference:

1. P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry, revised and expanded*, CRC Press, 1997.
2. S. W. Provencher, *Comput. Phys. Commun.*, 1982, 27, 229-242.
3. S. Aoki, T. Kurashina, Y. Kasahara, T. Nishijima and K. Nomiya, *Dalton Trans.*, 2011, 40, 1243-1253.