

【Electronic Supplementary Information】

The influence of ultrasound on porphyrin-based
metallogel formation: efficient control of H-and J-types
aggregations

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Experimental Section

General considerations: IR spectra were obtained for KBr pellets, in the range 400 - 4000 cm^{-1} , with a shimadzu FT-IR 8400S instrument. The optical absorption spectra of the samples were obtained using a UV-vis spectrophotometer (Hitachi U-2900). All fluorescence spectra were recorded on a RF-5301PC spectrophotometer. The powder X-ray diffraction (XRD) measurements of the samples were recorded on a Bruker D8-Advance X-ray powder diffractometer using Cu K α radiation ($\lambda = 0.1542$ nm) with scattering angles (2θ) of 3–70 $^\circ$, operating at 40 keV, cathode current of 20 mA.

Preparation of metallogel: In a vial, **1** (2 wt%) was added to Pd $^{2+}$ (0-4 equivalents) solution in acetonitrile. The resulting reaction mixture was exposed to ultrasonication (0.45 W/ cm^2 , 40 kHz) for 10 sec. After sonication, the reaction mixture formed a metallogel at room temperature. The metallogel was characterized by transmission electron microscopy (TEM), UV-vis spectroscopy, FT IR, XRD and rheometry.

TEM observation: For transmission electron microscopy (TEM), a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after one min, leaving some small patches of sample on the grid. The specimens were examined with a JEOL JEM-2010 transmission electron microscope operating at 200 kV using an accelerating voltage of 100 kV and a 16 mm working distance.

Photophysical studies: UV-Vis absorption and emission spectra of both the metallogel **1** and complex **1** with Pd $^{2+}$ obtained by ultrasound or heating, respectively in acetonitrile in the range of 200-800 nm. The absorption properties of gel **1** were studied extensively. UV/vis absorption spectra of gel **1** (2.0 wt%) were observed in the presence of Pd $^{2+}$ (0-4 equiv) in acetonitrile.

Rheological measurements: These were carried out on freshly prepared gels using a controlled stress rheometer (AR-1000N, TA Instruments Ltd., New Castle, DE, USA). Parallel plate geometry of 40 mm diameter and 1.5 mm gap was employed throughout. Following loading, the exposed edges of samples were covered with a silicone fluid from BDH (100 cs) to prevent water loss. Dynamic oscillatory work kept a frequency of 1.0 rad s $^{-1}$.

The following tests were performed: increasing amplitude of oscillation up to 100 % apparent strain on shear, time and frequency sweeps at 25 °C (60 min and from 0.1–100 rad s⁻¹, respectively) and a heating run to 90 °C at a scan rate of 1.0 °C min⁻¹. Unidirectional shear routines were performed at 25 °C covering a shear-rate regime between 10⁻¹ and 10³ s⁻¹. Mechanical spectroscopy routines were completed with transient measurements. In doing so, the desired stress was applied instantaneously to the sample and the angular displacement was monitored for 60 min (retardation curve). After completion of the run, the imposed stress was withdrawn and the extent of structure recovery was recorded for another 60 min (relaxation curve). Dynamic and steady shear measurements were conducted in triplicate and creep (transient) measurements in duplicate.

Preparation of single crystal of 1-Pd²⁺ complex: **1** (10 mmol) was added to Pd²⁺ (1.0 equiv) solution in DMF. Thus the reaction of **1** with K₂PdCl₄ in aqueous DMF solution was allowed to heat at 70 °C for 2 days. After cooling to room temperature, we obtained a red complex as single crystals suitable for X-ray analysis.

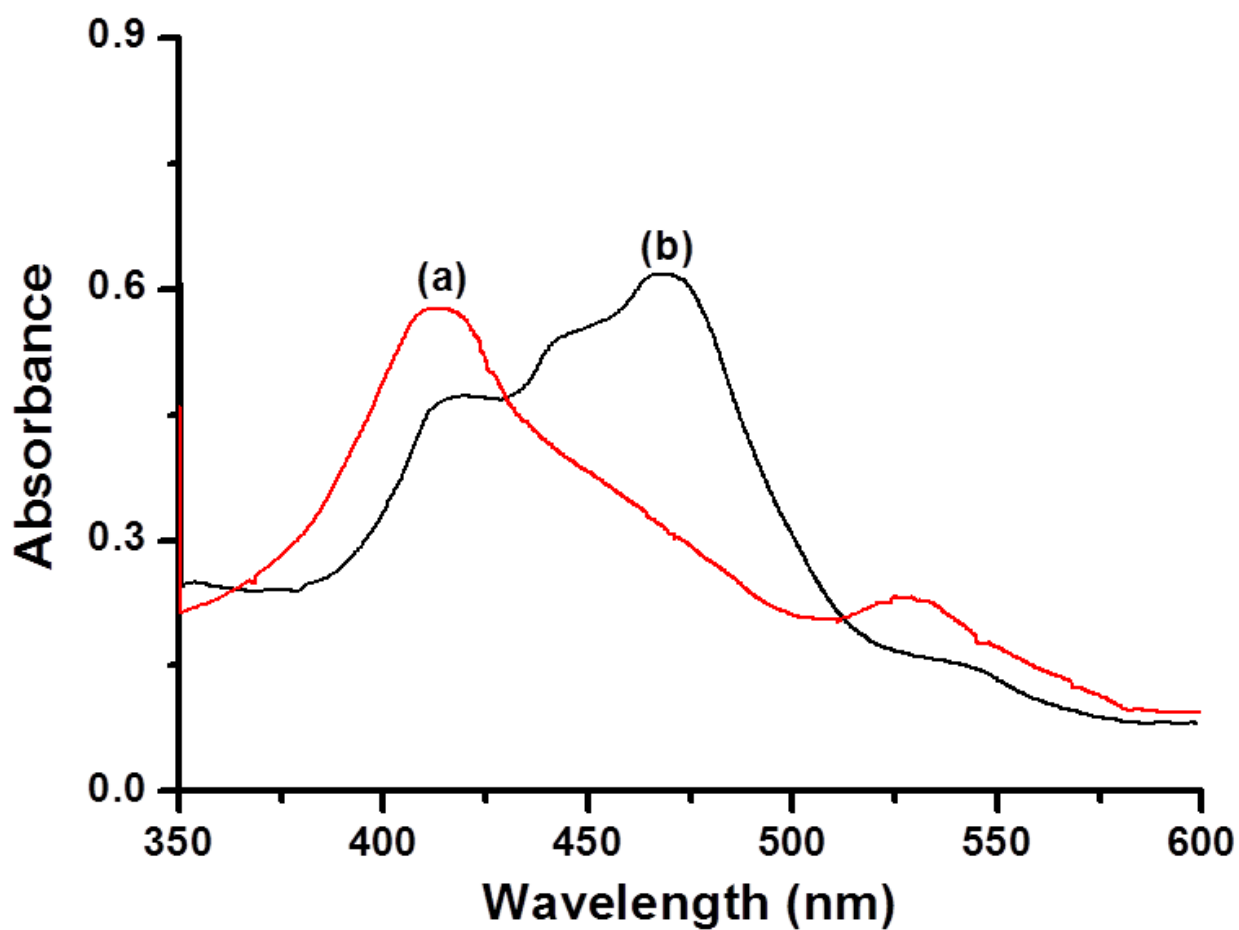


Fig. S1 UV-vis spectra of **1** (1.5 wt%) in the presence of Pd²⁺ (1.0 equiv) observed after (a) repeated ultrasound (b) heating to reversibility.

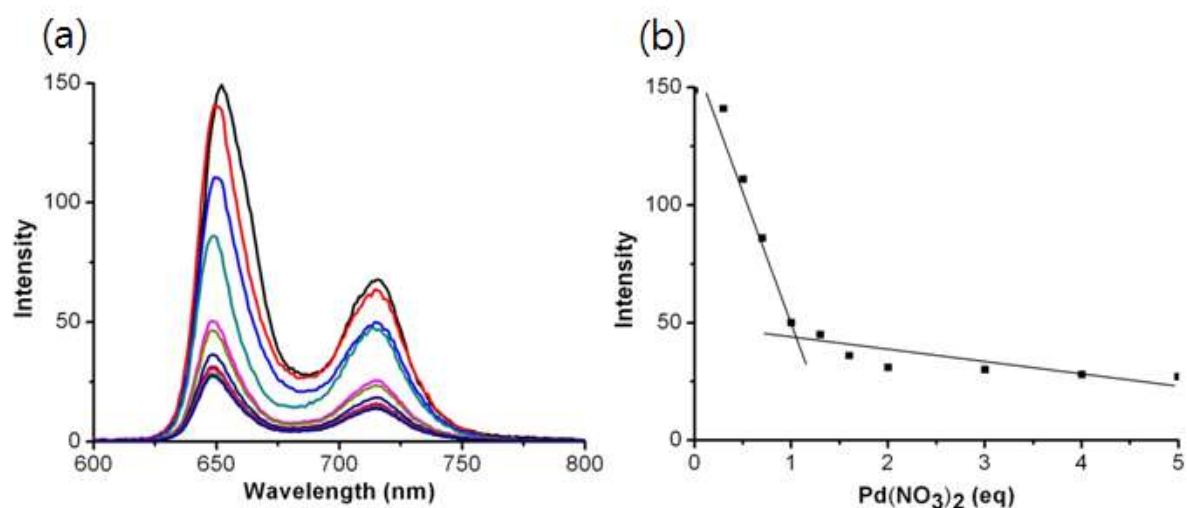


Fig. S2 (a) Fluorescence responses of Pd²⁺-porphyrin metallogel **1** (10 mM) upon addition of increasing Pd²⁺ ion concentrations (0, 0.3, 0.5, 0.7, 1.0, 1.3, 1.6, 2.0, 3.0, 4.0, 5.0 equiv; in acetonitrile ($\lambda_{\text{ex}} = 402$ nm)). (b) Plot of fluorescence intensity of Pd²⁺-porphyrin metallogel **1** against Pd²⁺ ion concentrations.

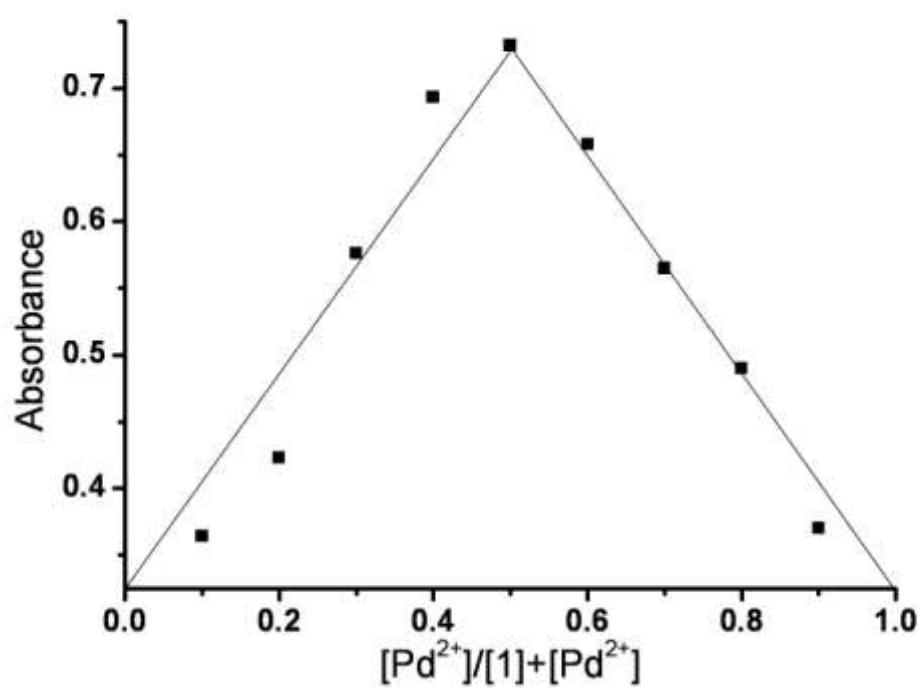


Fig. S3 Job's plot of 1:1 complex of Pd²⁺-porphyrin metallogel **1** (10 μM) in acetonitrile with ultrasound for 10 second. □

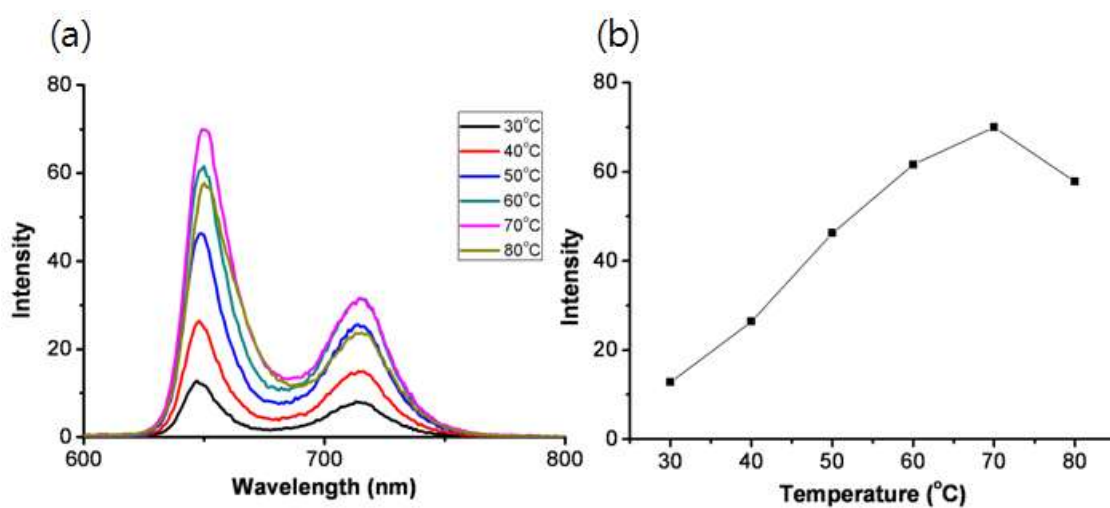


Fig. S4 (a) Fluorescence spectra of Pd²⁺-porphyrin metallogel **1** by changing of temperatures. (b) Plot of fluorescence intensity of Pd²⁺-porphyrin metallogel **1** against temperatures.

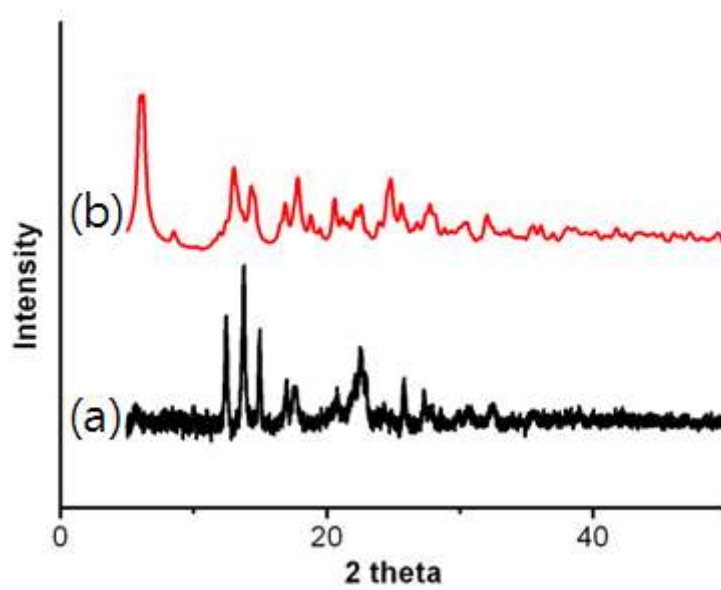


Fig. S5 Powder X-ray diffraction patterns of (a) Pd²⁺-porphyrin metallogel **1** obtained by ultrasound and (b) the solid **1**-Pd²⁺ obtained by heating.

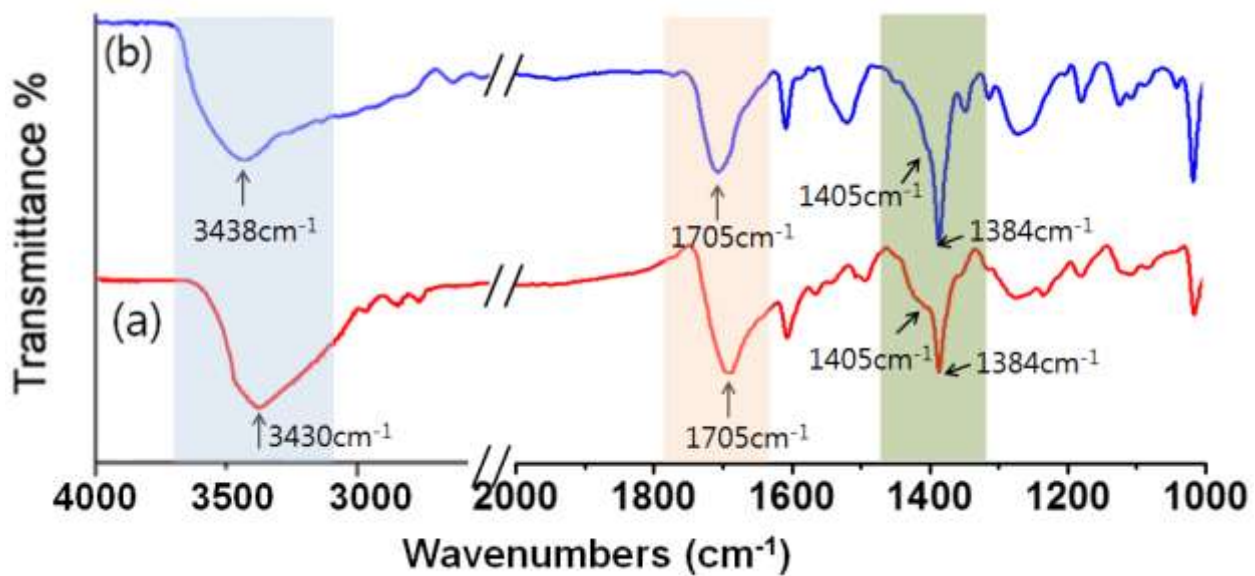


Fig. S6 FT IR spectra of Pd²⁺-porphyrin metallogel **1** obtained by (a) ultrasound and (b) 1-Pd²⁺ complex obtained by heating.

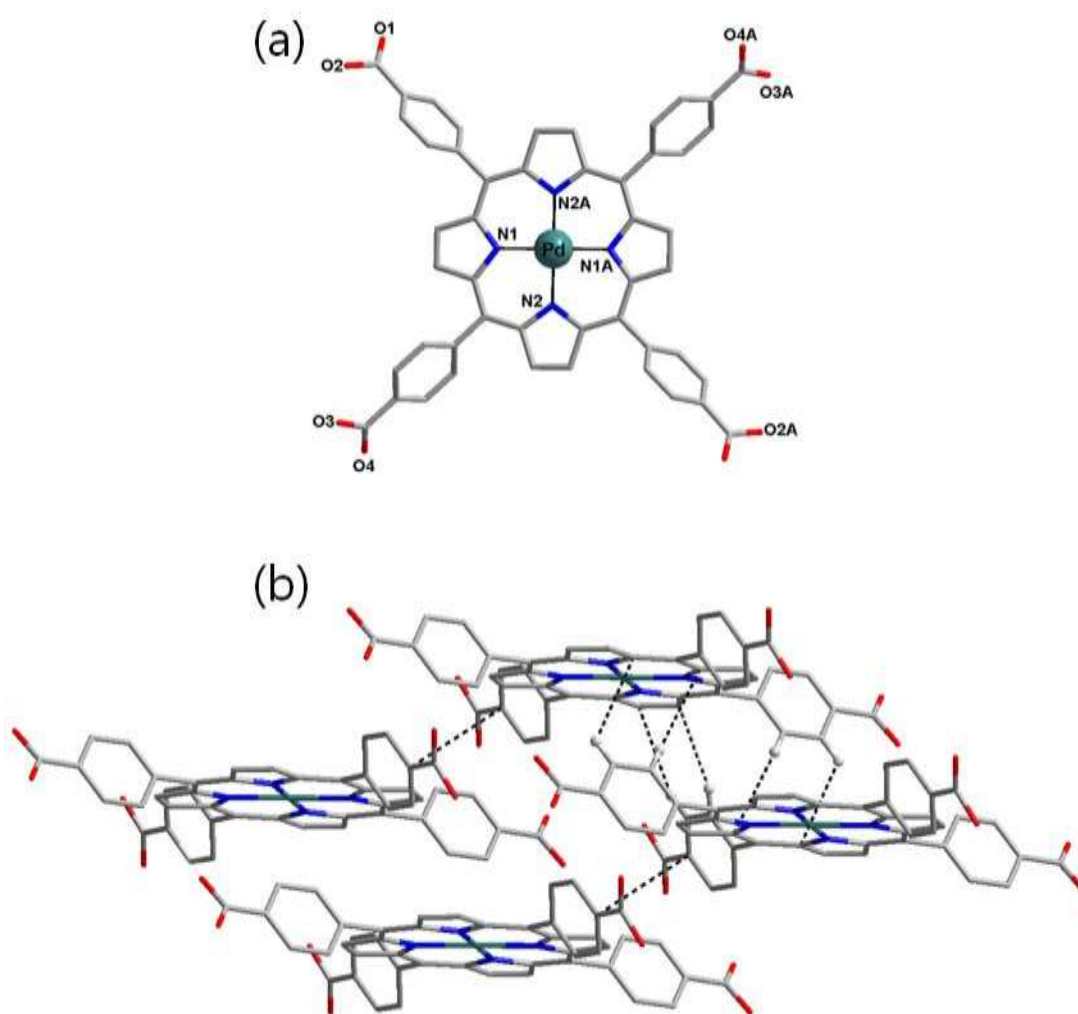


Fig. S7 (a) Asymmetric unit of $[\text{Pd}(\text{H}_4\text{X})]_2\text{DMF}\cdot\text{O}(\text{CH}_3\text{CH}_2)_2$. Hydrogen and solvent atoms are omitted. (b) Packing diagram, showing CH- π interaction (dashed lines). $\text{C}_{68}\text{H}_{74}\text{N}_8\text{O}_{14}\text{Pd}$, $M = 1333.75$, triclinic, $a = 7.6902(7) \text{ \AA}$, $b = 14.2290(15) \text{ \AA}$, $c = 14.8521(15) (6) \text{ \AA}$, $\alpha = 91.645(5)^\circ$, $\beta = 90.598(5)^\circ$, $\gamma = 90.643(5)^\circ$, $U = 1624.3(3) \text{ \AA}^3$, $T = 173(2) \text{ K}$, space group P-1, $Z = 1$, $\mu(\text{Mo K}\alpha) = 0.357 \text{ mm}^{-1}$, 6226 reflections measured, 8741 unique ($R_{\text{int}} = 0.0415$) which were used in all calculations. The final $wR(F_2)$ was 0.1230 (all data).

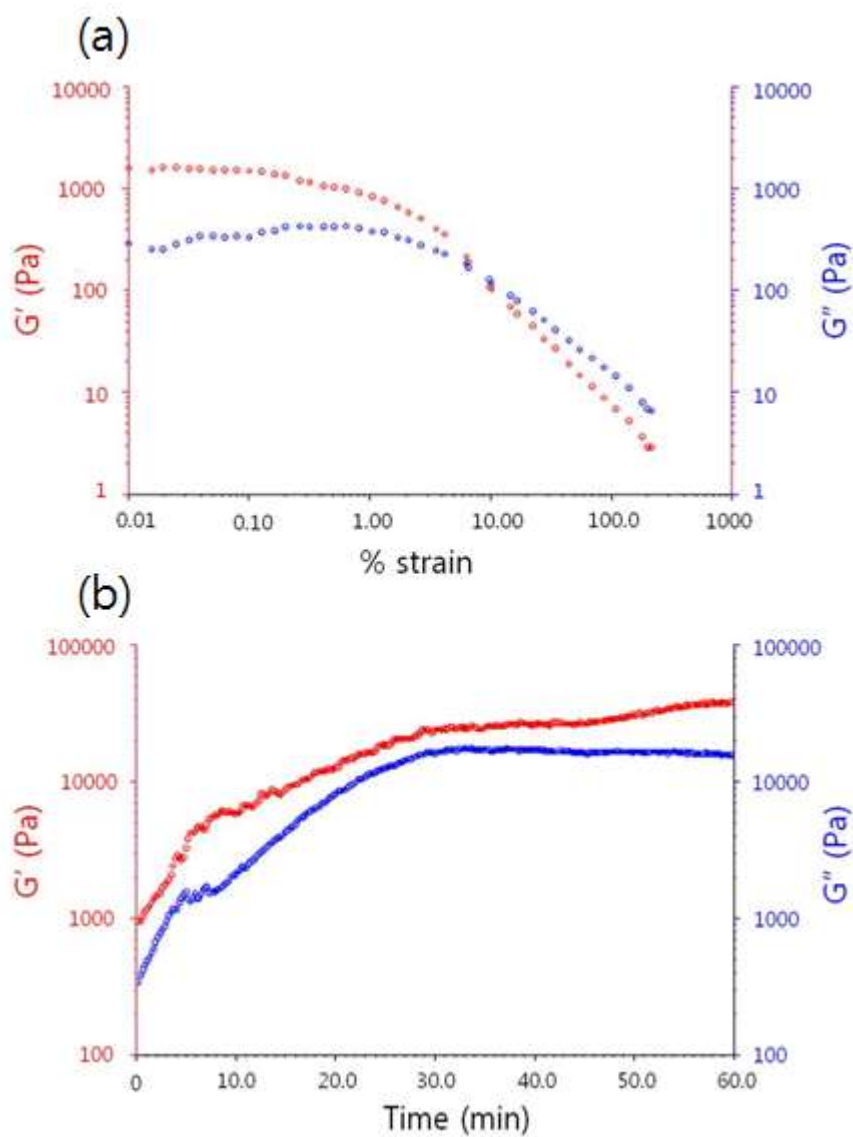


Fig. S8 (a) Frequency sweep of G' and G'' for Pd²⁺-porphyrin metallogel **1** at a strain of 0.1 %. (b) Temperature ramp G' and G'' for Pd²⁺-porphyrin metallogel **1** at the heating rate of 1 °C min⁻¹, strain of 0.1 % and frequency of 1 rad s⁻¹.