

Electronic supplementary information (ESI)

Pyridine-based coordination polymer hydrogel with Cu²⁺ ion and its encapsulation for hydrophobic molecule

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Experimental sections

^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 apparatus. IR spectra were obtained for KBr pellets, in the range $400 - 4000\text{cm}^{-1}$, with a shimadzu FT-IR 8400S instrument, and Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained by using a UV-vis spectrophotometer (Hitachi U-2900). All fluorescence spectra were recorded in RF-5301PC spectrophotometer.

TEM and SEM observations. 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 the 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. Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5–15 kV and the emission current was $10\ \mu\text{A}$.

Photophysical studies: UV-Vis absorption and emission spectra of the gel at each temperatures and dispersed in water in the range of 200-800nm. The absorption properties of gel **1** were studied extensively. UV/vis absorption spectra of gel **1** ($[\mathbf{1}] = 20\ \text{mM}$) were observed in the presence of Cu^{2+} (0-5 equiv.).

General procedure for preparation of metal coordination polymeric gel: In a vial, the solution of metal salt [$200\ \mu\text{L}$, 3 equiv.] was added to solution of ligand [$100\ \mu\text{L}$, 1~5 wt % in H_2O]. The metal coordination polymeric gel is formed immediately upon neutral condition ($\text{pH} = 7$). The resulting reaction mixture was allowed to sonicate. The gelation state of the material was evaluated by “stable-to-inversion” of the test tube.

Preparation and characterization of curcumin container with gel inside and release test.

5% of curcumin was dissolved in a 2.5 wt% hydrogels. The mixture was kept in the form of liquid by maintaining the temperature above its gelation until completion of sonication. The release of drugs from hydrogels was performed in a pH solution. 1 mL of pH solution was layered on top of 2.5 wt% gel in a vial. The release experiments were conducted at a controlled pH. After 80 min, a yellow solution was obtained. During the release, pH solution on the hydrogel was taken out at a desired period and subjected to UV-vis measurement. The quantitative analysis of curcumin was based on UV-vis data since the intensity of the peaks is dependent on the concentration of curcumin.

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). 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.

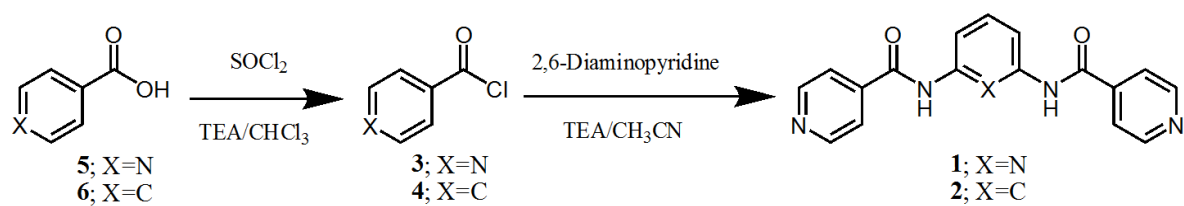
Preparation of compound 1: *N,N'*-Bis(4-pyridylcarbonyl)-2,6-diaminopyridine (1)¹. Thionyl chloride (11.89 g, 100 mmol) was added dropwise to isonicotinic acid (12.31 g, 100

mmol) and triethylamine (10.11 g, 100 mmol) in chloroform. The mixture was refluxed for 2 h and cooled down to room temperature. Then an acetonitrile solution of diaminopyridine (5.45 g, 50 mmol) and triethylamine (10.11 g, 100 mmol) were added dropwise to the resulting isonicotinyl chloride solution, cooled by salt and ice water. The solution was stirred for 12 h, and then water was added. From the resulting solution, yellow powder was filtered and washed with a dilute Na₂CO₃ solution, distilled water, and then a small amount of cold methanol. The product **1** was obtained as yellowish white powder (8.88 g, 55.8%). ¹H NMR (300 MHz, DMSO-d₆): δ 10.93 (s, 2H NHCO), δ 8.78 (dd, 4H NCH), δ 7.89 (dd, 4H CCH), δ 7.9 (m, 3H CHCHCHC). ¹³C NMR (75.4 MHz, DMSO-d₆): δ 165.5, 150.8, 150.3, 141.5, 122.3, 112.5. HRMS (*m/z*) Calcd. for C₁₇H₁₃N₅O₂: 319.1069. Found: 319.1086 (M⁺).

Compound 2: Compound **2** was prepared by previous reported a method.¹

Reference

- 1) T. H. Kim, J. Seo, S. J. Lee, S. S. Lee, J. Kim and J. H. Jung, *Chem. Mater.*, 2007, **19**, 5815-5817.



Scheme S1. Synthetic route of ligands **1** and **2**.

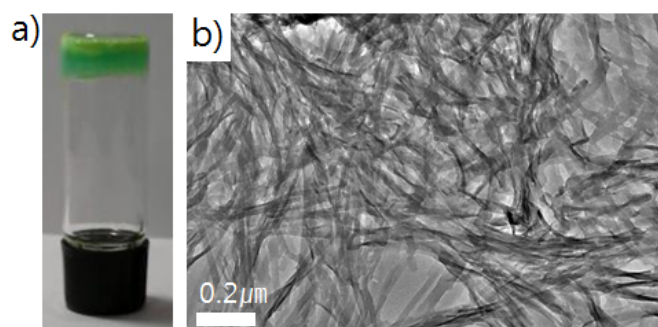


Fig. S1 (a) photograph and TEM image of Cu^{2+} coordination polymeric gel **2** (20 mM) at pH = 7.

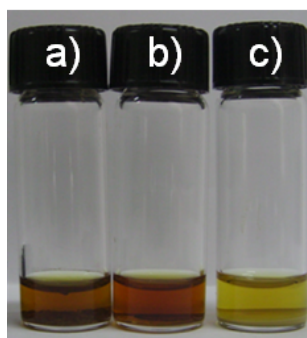


Fig. S2 Photograph of **1** (20 mM) with (a) Mn^{2+} , (b) Co^{2+} , (c) Zn^{2+} ions (3.0 equiv) at pH=7.

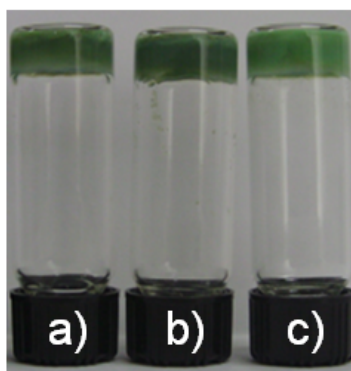


Fig. S3 Photographs of hydrogels **1** (20 mM) in the presence of Cu^{2+} (3 equiv); (a) NO_3^- , (b) Cl^- and (c) SO_4^{2-} at pH=7.

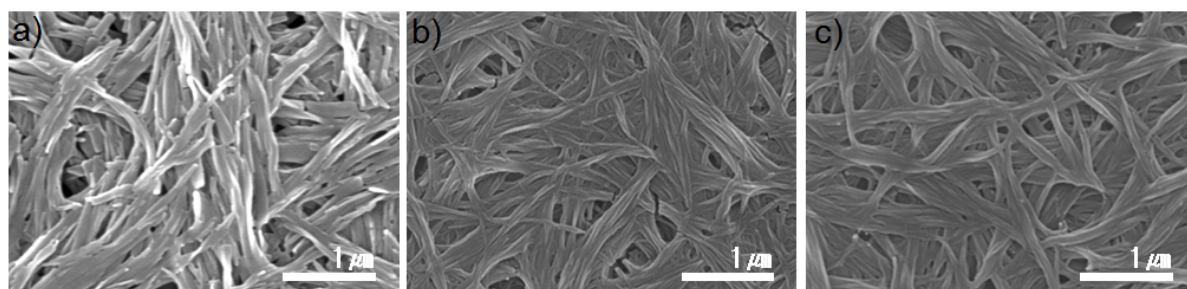


Fig. S4 SEM images of Cu^{2+} coordination hydrogel **1** with different anions; (a) $\text{Cu}(\text{NO}_3)_2$, (b) CuCl_2 and (c) CuSO_4 .

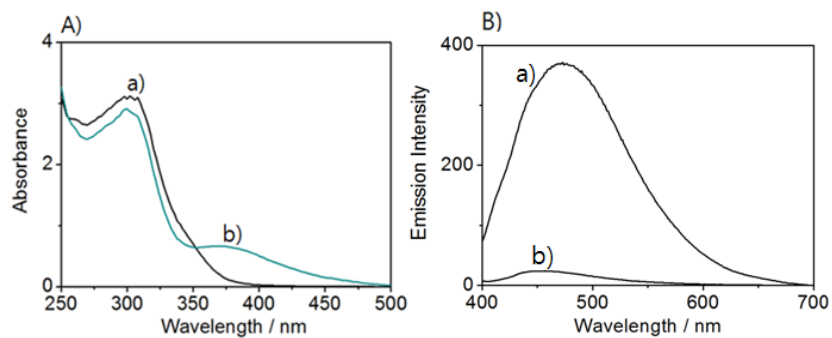


Fig. S5 (A) UV-vis spectra of (a) sol **1** (20 mM) without Cu²⁺ and (b) gel **1** (20 mM). (B) Fluorescence spectra of (a) sol **1** (20 mM, λ_{ex}=380nm) without Cu²⁺ and (b) gel **1** (20 mM, λ_{ex}=380 nm) with Cu²⁺ (3equiv).

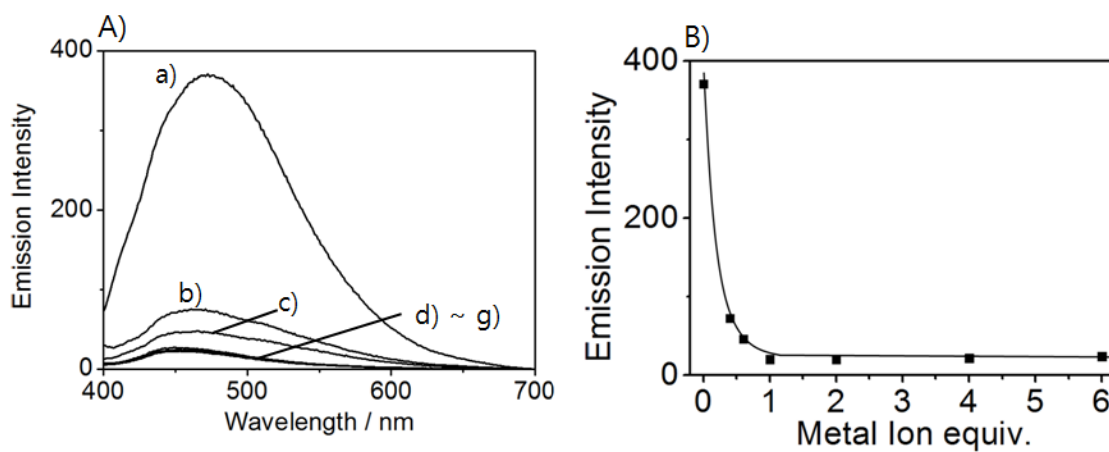


Fig. S6 A) Fluorescence spectra of a) sol **1** (20 mM, $\lambda_{\text{ex}}=302$ nm) without Cu^{2+} and gel **1** (20 mM) with Cu^{2+} (b) 0.25, (c) 0.5, (d) 1, (e) 2, (f) 4 and (g) 6 equiv. B) Fluorescence intensity changes of the hydrogel **1** upon the addition of Cu^{2+} at pH=7.

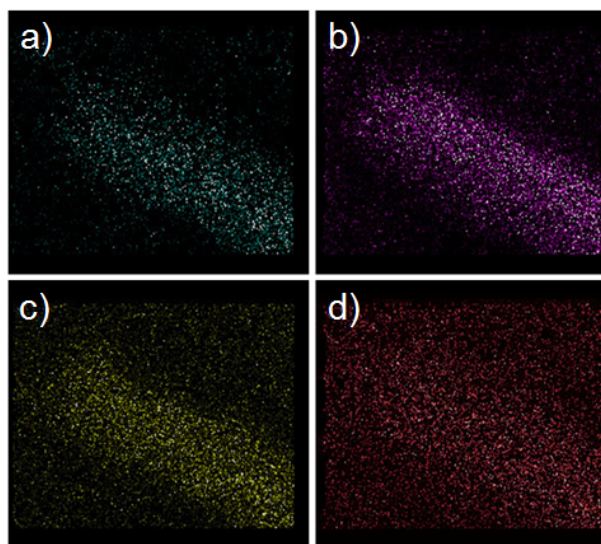


Fig. S7 TEM image of hydrogel **1** with Cu^{2+} corresponding elemental mapping images of (a) Cu, (b) C, (c) N and (d) O.

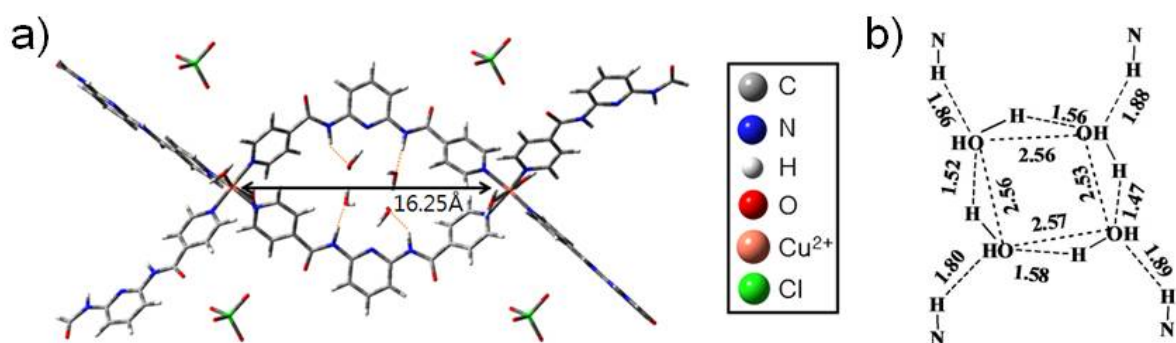


Fig. S8 a) The B3LYP/3-21G* optimized structure for the Cu²⁺-ligand **1**. b) Hydrogen bonding networks around the cyclic water tetramer inside the cavity of the Cu²⁺ - **1** complex.

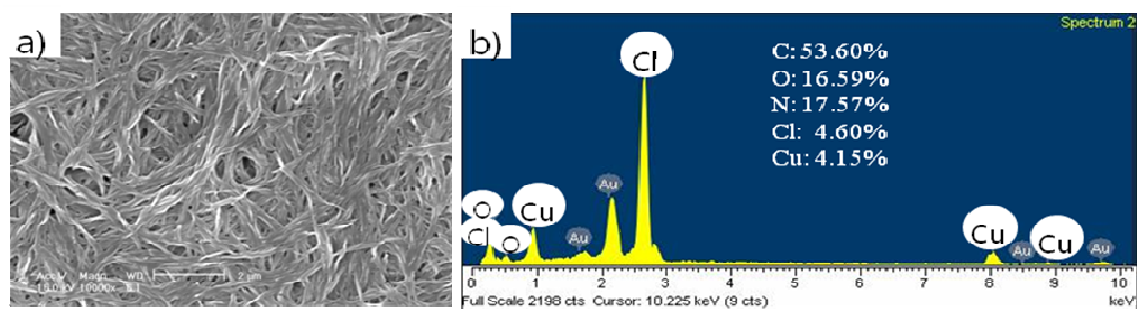


Fig. S9 (a) X-ray electron probe microanalyzer (EPMA) image and (b) EDX analysis of Cu^{2+} coordination polymeric gel **1**.

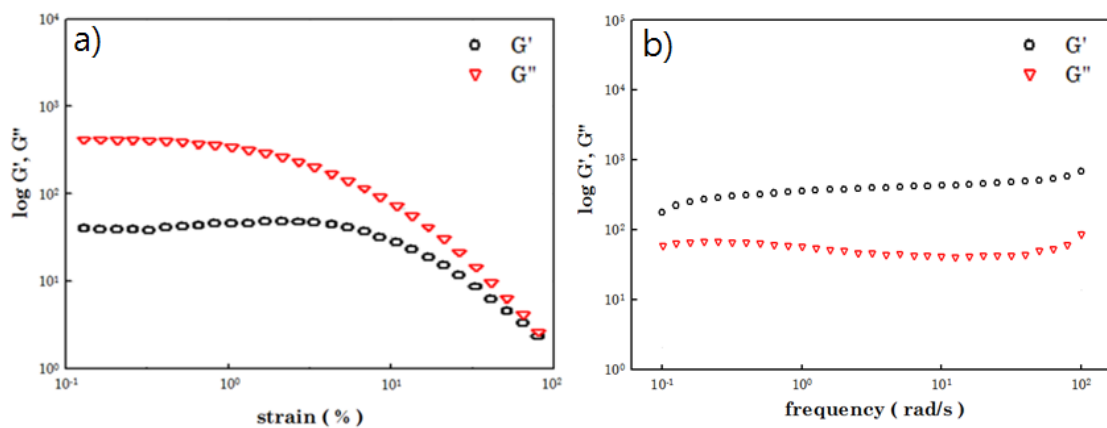


Fig. S10 (a) Strain sweep at a frequency of 1 rad s^{-1} of 2.5 wt% of Cu^{2+} coordination polymeric gel **1** at strain of 0.1 % and frequency of 1 rad s^{-1} . (b) Frequency sweep of G' and G'' for Cu^{2+} coordination polymeric gel **1** at a strain of 0.1 %.

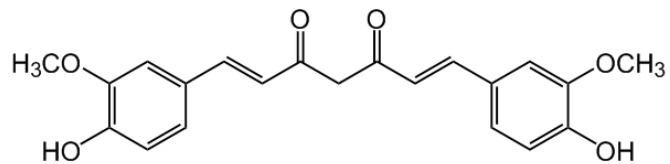


Fig. S11 Chemical structure of curcumin.

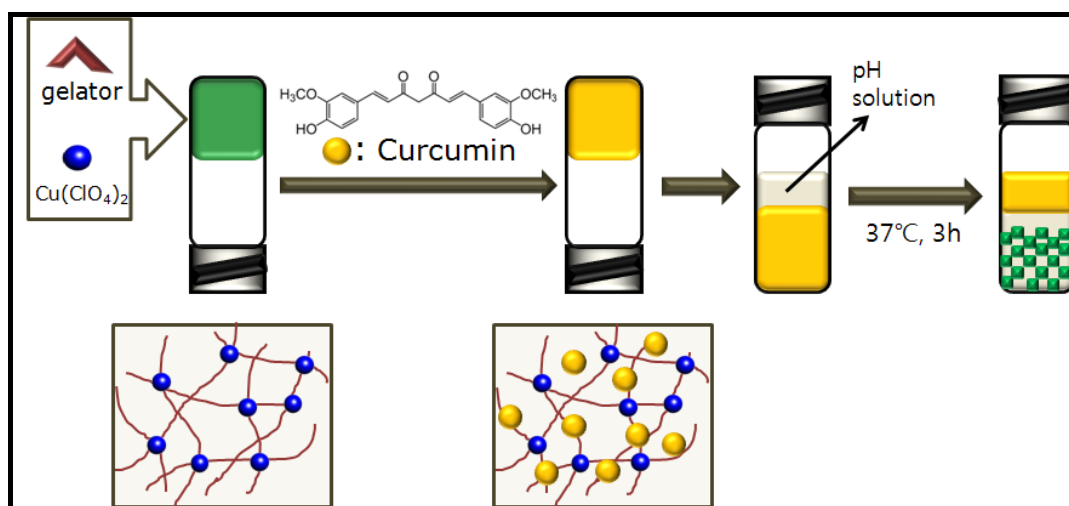


Fig. S12 Schematic representation of curcumin encapsulation and release in hydrogel 1 with Cu^{2+} by change of pH value.

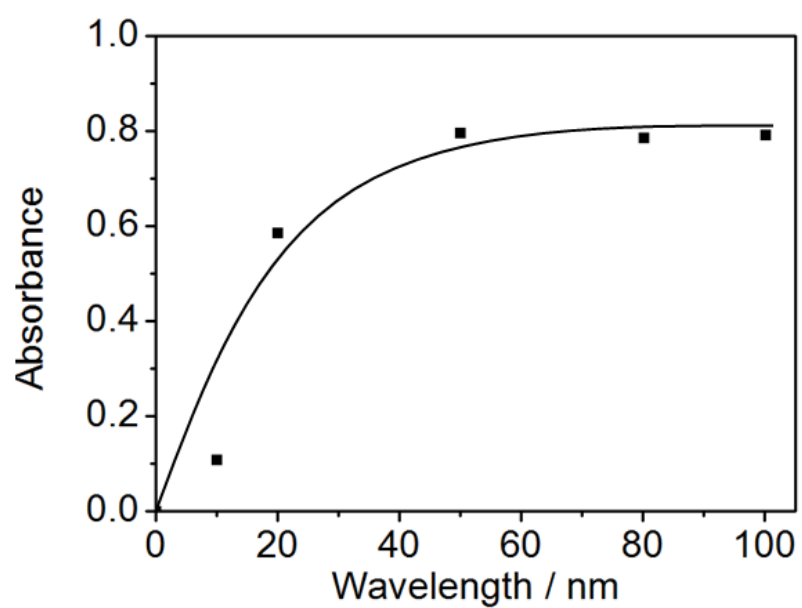


Fig. S13 Response curve for UV/Vis spectra of curcumin released from hydrogel **1** - curcumin gel with Cu^{2+} by change of times.