Electronic supplementary information (ESI)

Fluorescent hydrogels formed by CH–π and π–π interactions as main driving forces: an approach toward understanding the relationship between fluorescence and structure

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Experimental Section

General method: ^{1}H NMR spectra were measured on a Bruker ARX 300 apparatus. The FT-IR spectra of the compounds were measured with a Shimadzu FTIR-8400S spectrometer. and Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. For field emission scanning electron microscope (FE-SEM) a piece of compounds was placed on a carbon tape after gold coating, the specimen was then examined with JEOL JEM-2010. For Atomic force microscopy a piece of mica was prepared. Mica was fixed on the slide glass and diluted sample was dropped on the mica. and then, Sample was dried in air. Transmittance spectra were acquired with a Shimadzu UV-3600 double-beam UV/Vis/NIR spectrophotometer using standard 1 cm quartz curvets. Fluorescence spectra were recorded in RF-5301PC spectrophotometer. In addition, X-ray diffraction patterns of gel and crystal sample were measured with a rigaku diffractometer (Type4037) using graded *d* space elliptical side-by-side multilayer optics, monochromated Cu K radiation (40 Kv, 30 Ma) and an imaging plate (R-AxisIV).

Gelation test of 1 and 2: In a typical experiment, compound **1** (3.0 wt%) was dissolved in 1.0 N nitric acid (100 μL) and sodium hydroxide (100 μL) was added to dissolved solution. The mixture was dissolved by heating and left to cool to room temperature. Compound **2** (3.0 wt%) was dissolved in DMSO (100 μL). Then, water (100 μL) was added to solution. When the mixture appeared as a solid-like material, the container was inverted. The sample was considered to be a gel if it did not deform.

pH dependence of fluorescence hydrogels 1 and 2: To diluted nitric acid and sodium hydroxide solutions (50 mL) of different molar concentrations, compounds **1** or **2** (3 mg) were dissolved, and the pH of the mixture was measured. The excitation and emission spectra were corrected for the wavelength-dependent lamp intensity and detector response, respectively. The pulsed excitation source was generated using the 330 nm of the Xenon lamp for **1** or **2**.

Crystallographic structure determinations: Data for **1** data was collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. The frame data were processed to give structure factors using SAINT.[S1] The structure was solved by the direct method and refined by the full matrix least squares method on F^2 for all data using SHELXTL software.[S2]

Data for **2** was also collected on a Bruker SMART APEX2 ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package APEX2.[S3] All of the calculations for the structure determination were carried out using the SHELXTL package.[S4] The N1 and C5 atoms of **2** are disordered over two positions with occupancies of 0.51: 0.49.

Preparation of single crystals: 1 and **2** were prepared by evaporation from methanol or water solution containing equimolar amounts of hydrogen acceptor and donor moieties followed by drying *in vacuo*. For example, the 2/HNO_3 **1**/**2** salt was prepared by the mixture of **1** or **2** (0.016 g, 0.05 mmol) in methanol or water (2 mL), followed by drying *in vacuo* after it was concentrated methanol or water.

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 258C covering a shear-rate regime between 10^{-1} and 10^{-3} 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: Compound **1** was prepared by previous reported a method.[S5] 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 Na_2CO_3 solution, distilled water, and then a small amount of cold methanol. The product **L** was obtained as yellowish white powder (8.88 g, 55.8%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.93 (s, 2H NHCO), δ 8.78 (dd, 4H NCH), δ 7.89 (dd, 4H CCH), δ 7.9 (m, 3H CHCHCHC). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 165.5, 150.8, 150.3, 141.5 122.3 112.5. HRMS (*m/z*) Calcd. for $C_{17}H_{13}N_5O_2$: 319.1069. Found: 319.1086 (M^+).

Preparation of compound 2: Thionyl chloride (11.89 g, 100 mmol) was added dropwise to nicotinic 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 nicotinyl 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 saturated Na_2CO_3 solution, distilled water, and then a small amount of cold methanol. The product **2** was obtained as yellowish white powder (8.88 g, 55.8%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.09 (s, 2H NHCO), δ 8.78 (dd, 4H NCH), δ 7.89 (dd, 4H CCH), δ 7.9 (m, 3H CHCHCHC). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 165.5, 151.5, 150.0, 141.0 122.3 112.8. HRMS (*m/z*) Calcd. for $C_{17}H_{13}N_5O_2$: 319.1069. Found: 319.1086 (M^+). FT-IR: 3321, 3041.32 cm^{-1}, 3012.4, 1672.94, 1591.91, 1477.21, 1445.78, 1423.27 cm^{-1}, 1526.64, 1272.34, 1197.41 and 1240.2 cm^{-1}. Element analysis: calculated for $C_{17}H_{13}N_5O_2$: C 63.94 H 4.10 N 21.93 O 10.02 Found C 63.96 H 4.12 N 21.94

References

S1. Bruker, *SMART and SAINT: Area Detector Control and Integration Software (Ver. 5.0)*, Bruker Analytical X-ray Instruments: Madison, Wisconsin, USA (1998).

S2. Bruker, *SHELXTL: Structure Determination Programs (Ver. 5.16)*, Bruker Analytical X-ray Instruments: Madison, Wisconsin, USA (1998).

S3. Bruker, *APEX2 (Version 2009.1-0), Data Collection and Processing Software*, Bruker AXS Inc., Madison, Wisconsin, U.S.A. (2008).

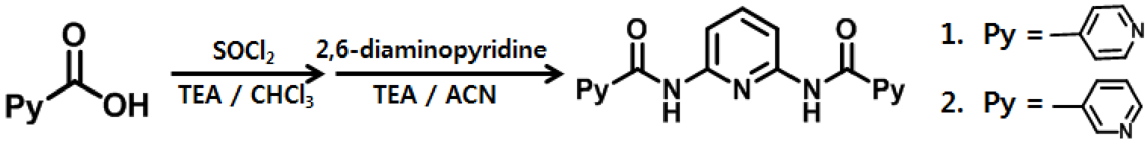
S4. Bruker, *SHELXTL-PC (Version 6.22)*, *Program for Solution and Refinement of Crystal Structures*, Bruker AXS Inc., Madison, Wisconsin, USA (2001).

S5. T. H. Kim, J. Seo, S. J. Lee, S. S. Lee, J. Kim and J. H. Jung, *Chem. Mater.*, 2007, **19**, 5815.

Table S1. Gelation abilities of gelators **1** and **2**.

solvent	Phase	
	Gelator **1**	Gelator **2**
Water (pH = 7)	G	PG
Water (pH = 2)	S	PG
Methanol	S	S
Ethanol	S	S
Methylene chloride	S	
Chloroform	S	PG
Tetrahydrofuran	S	S
Methyl cyanate	I	I
Cyclohexane	I	
Toluene	I	I
p-Xylene	I	
Benzylachol	I	S
Dimethyl sulfoxide(DMSO)	S	S
Methanol and Chloroform (1:1)	S	S
Ethyl acetate	I	I
Butanol	S	S
Acetone	I	I
Acetonitrile	I	I
Pyridine	S	S
DMSO/Water (1:1 v/v)	S	G

Scheme S1. Synthetic methods of **1** and **2**.



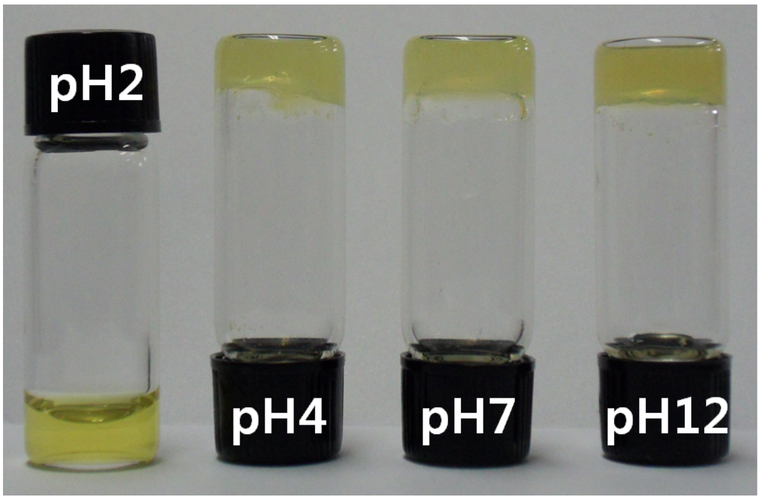


Fig. S1 The photograph of hydrogel **1** prepared from water.

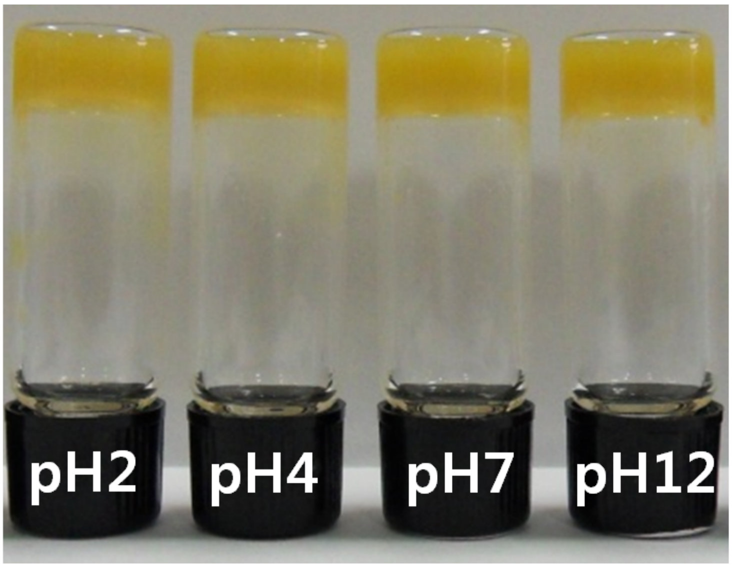


Fig. S2 The photograph of hydrogel **2** prepared from DMSO/water(1:1 v/v).

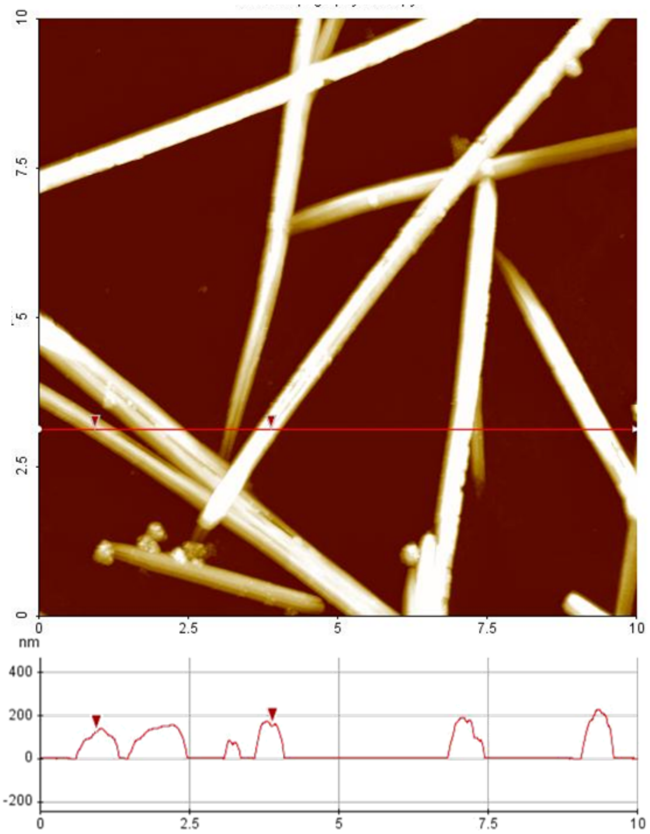


Fig. S3 AFM image of hydrogel **1** prepared from water at pH 7 and its profile for height.

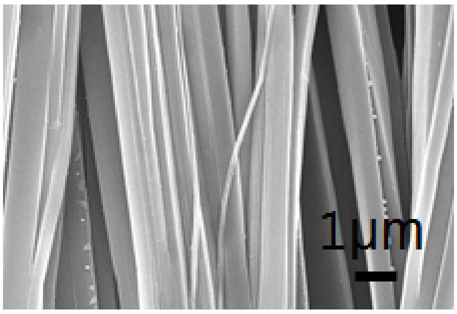


Fig. S4 SEM image of hydrogel **1** prepared from water at pH 12.

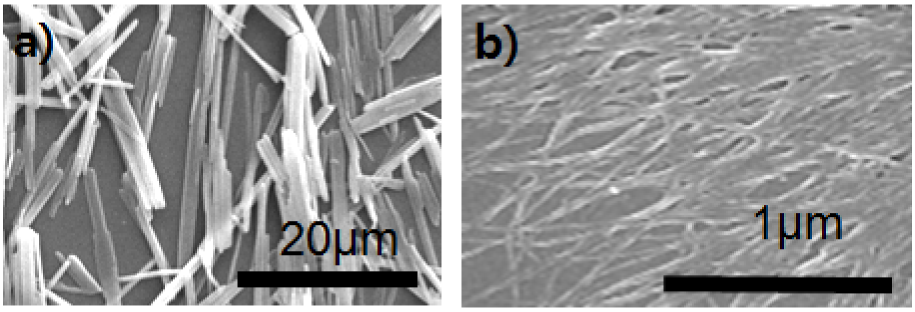


Fig. S5 SEM images of hydrogel **2** prepared from DMSO/water(1:1 v/v) at pH (a) 2 and (b) 12.

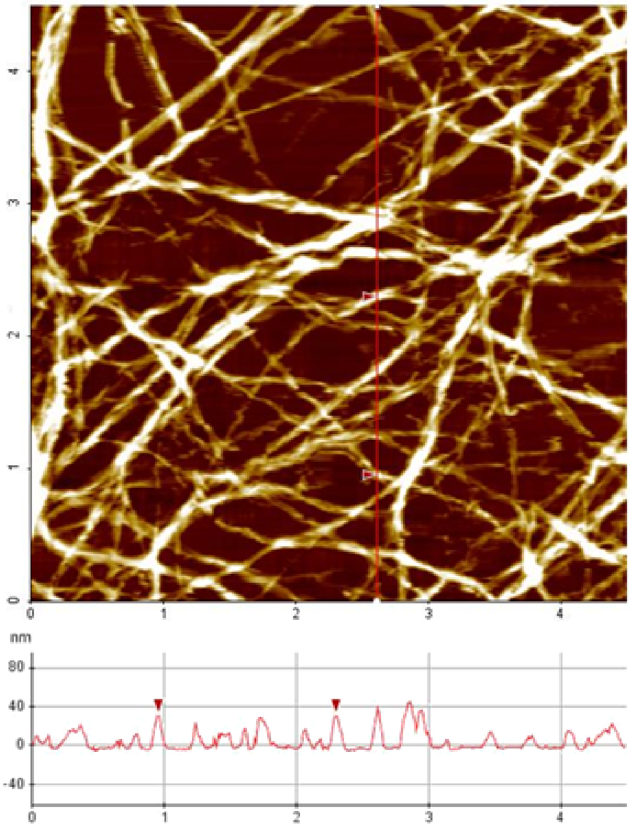


Fig. S6 AFM image of hydrogel **2** prepared from DMSO/water(1:1 v/v) at pH 7 and its profile for height.

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Table S2. Crystal and experimental data.

	1	**2**
Formula	$C_{17}H_{13}N_5O_2$	$C_{34}H_{26}N_{10}O_4$
Formula weight	319.32	638.65
Temperature (K)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Z	4	4
a (Å)	17.1841(9)	8.3304(6)
b (Å)	12.4648(7)	16.7637(12)
c (Å)	6.7661(4)	20.9646(15)
α (°)		90
β (°)		92.043(4)
γ (°)		90
V (Å^3)	1449.27(14)	2925.8(4)
D_x (g/cm^3)	1.463	1.450
$2\theta_{max}$ (°)	56.58	56.80
R	0.0718	0.0566
wR	0.1438	0.1047
No. of reflection used [> $2\sigma(I)$]	3229	7310
Diffractometer	Bruker SMART CCD system	Bruker SMART APEX2 ULTRA
Structure determination	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix

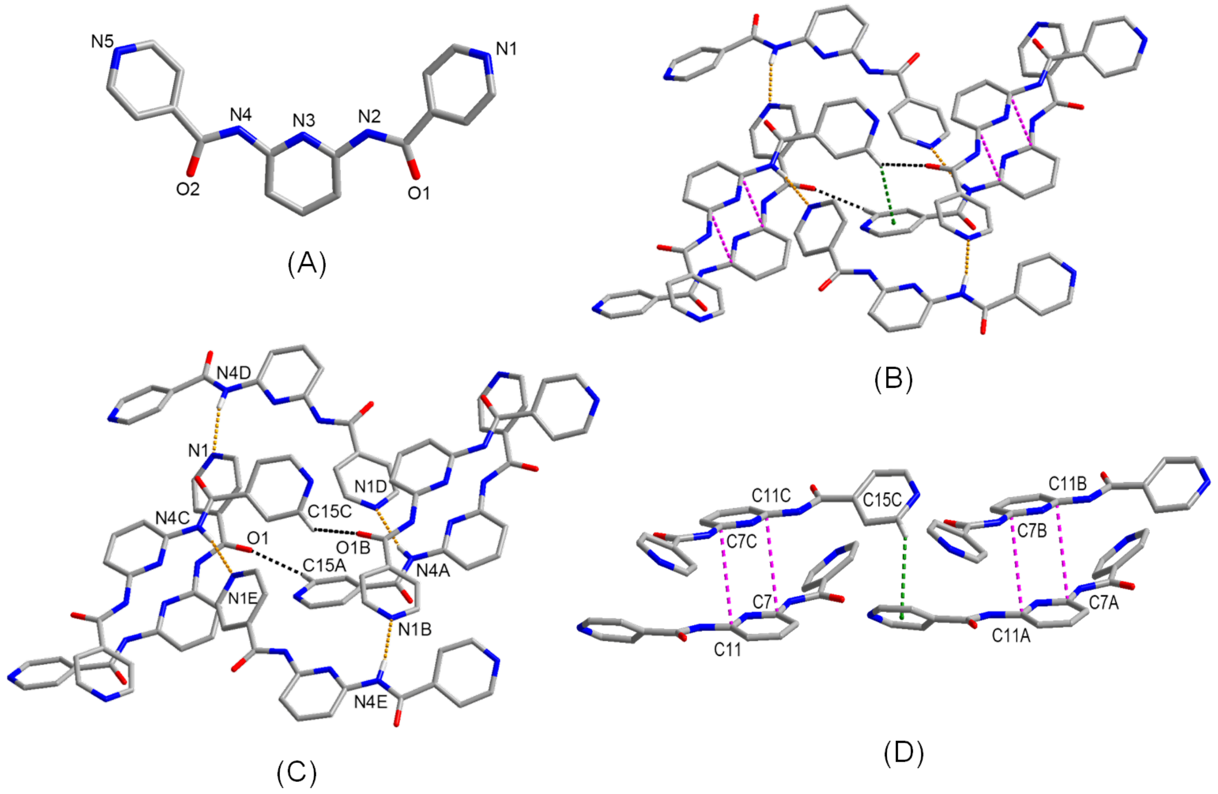

Fig. S7 The asymmetric unit of (A) **1** and (B) packing structure of **1** sustained by N-H···N (yellow dashed lines), C-H···O (black dashed lines) (C), π···π (pink dashed lines) and C-H···π (green dashed lines) bonds (D). Symmetry codes for **1**: A: *x*, -1+*y*, *z*; B: 0.5-*x*, -1-*y*, -0.5-*z*; C: 0.5-*x*, -*y*, -0.5+*z*; D: -*x*, -0.5+*y*, 1.5-*z*; E: 0.5+*x*, -0.5-*y*, 1-*z*.

Table S3. Geometrical parameters of hydrogen bonds in crystal **1**.

D-H···A	D-H(Å)	H···A (Å)	D···A (Å)	D-H···A (deg)	Symmetry –for-A
N4-H4N···N1	0.88	2.29	3.151(4)	167	-*x*, 0.5+*y*, 1.5-*z*
C2-H2···N3	0.95	2.64	3.275(4)	125	-*x*, -0.5+*y*, 1.5-*z*
C3-H3···N5	0.95	2.76	3.359(5)	122	-0.5+*x*, 0.5-*y*, 2-*z*
C14-H14···N1	0.95	2.60	3.280(5)	129	-*x*, 0.5+*y*, 1.5-*z*
C15-H15···O1	0.95	2.53	3.247(4)	133	*x*, 1+*y*, *z*

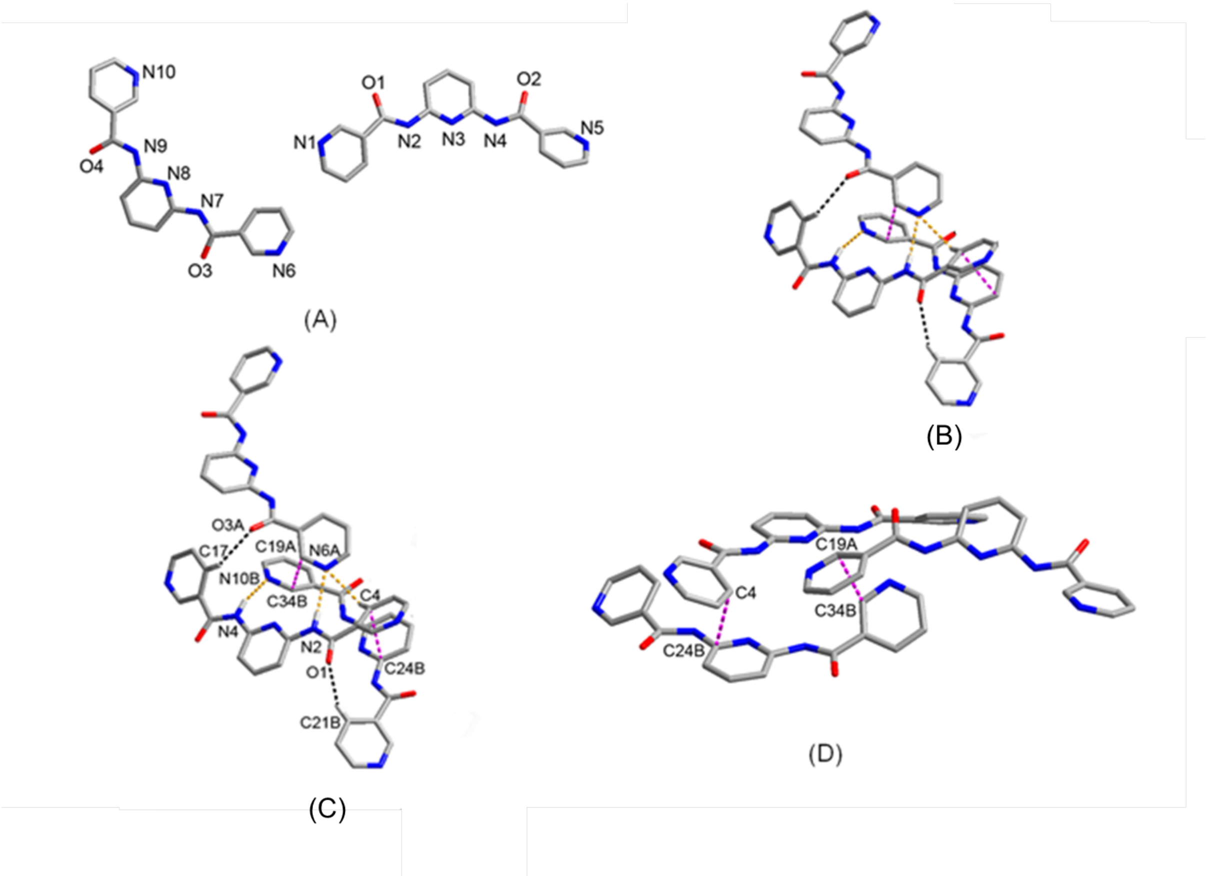

Fig. S8 The asymmetric unit of (A) **2** and (B) packing structure of **2** sustained by N-H···N (yellow dashed lines), N-H···O (brown dashed lines), C-H···O (black dashed lines) (C) and π···π (pink dashed lines) bonds (D). Symmetry codes for **2**: A: 1-*x*, 1-*y*,1- *z*; B: 1-*x*, 0.5+*y*, 0.5-*z*; C: *x*, 0.5-*y*,0.5+-*z*.

Table S4. Geometrical parameters of hydrogen bonds in crystal **2**.

D-H···A	D-H(Å)	H···A (Å)	D···A (Å)	D-H···A (deg)	Symmetry –for-A
N2-H2A···N6	0.86	2.41	3.270(3)	149	1-*x*, 1-*y*, 1-*z*
N4-H4A···N10	0.86	2.25	3.011(3)	149	1-*x*, 0.5+*y*, 0.5-*z*
N7-H7A ···N5	0.86	2.14	2.966(2)	162	-1+*x*, 1.5-*y*, -0.5+*z*
N9-H9A ···O2	0.86	2.29	3.111(2)	159	-1+*x*, 1.5-*y*, -0.5+*z*
C4-H4B···N6	0.93	2.55	3.237(3)	131	1-*x*, 1-*y*, 1-*z*
C9-H9B···O3	0.93	2.50	3.248(3)	137	*x*,1+ *y*, *z*
C14-H14A···N8	0.93	2.58	3.230(3)	128	1+*x*, 1.5-*y*, 0.5+*z*
C21-H21A···O1	0.93	2.49	3.265(3)	141	1-*x*, -0.5+*y*,0.5- *z*
C21-H21A···N5	0.93	2.69	3.102(3)	108	-1+*x*, 1.5-*y*, -0.5+*z*
C26-H26A···O4	0.93	2.69	3.181(3)	114	-*x*, -*y*,- *z*

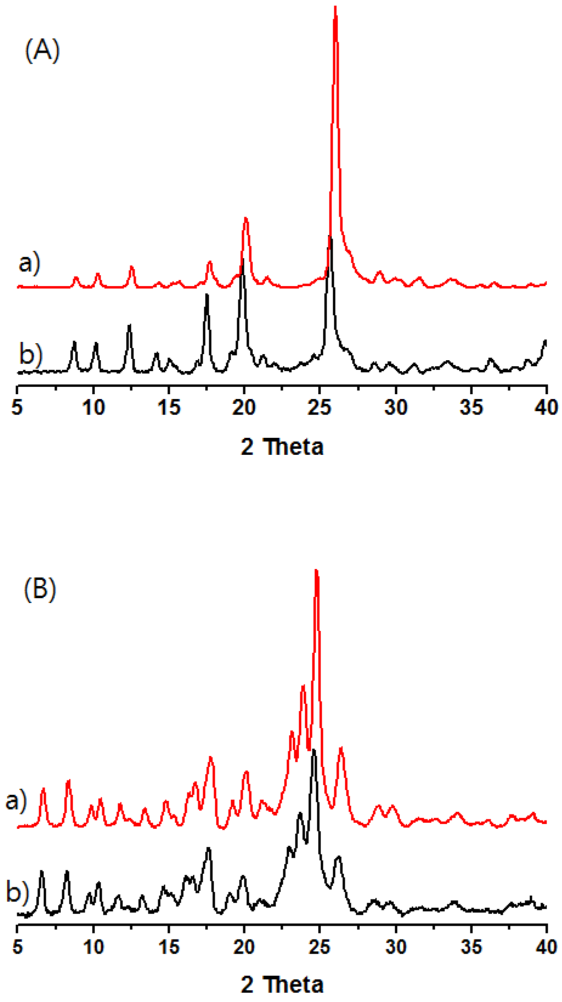

Fig. S9 XRD patterns of (A) (a) xerogel **1** and (b) bulk crystal **1** and (B) xerogel **2** and (b) bulk crystal **2**.

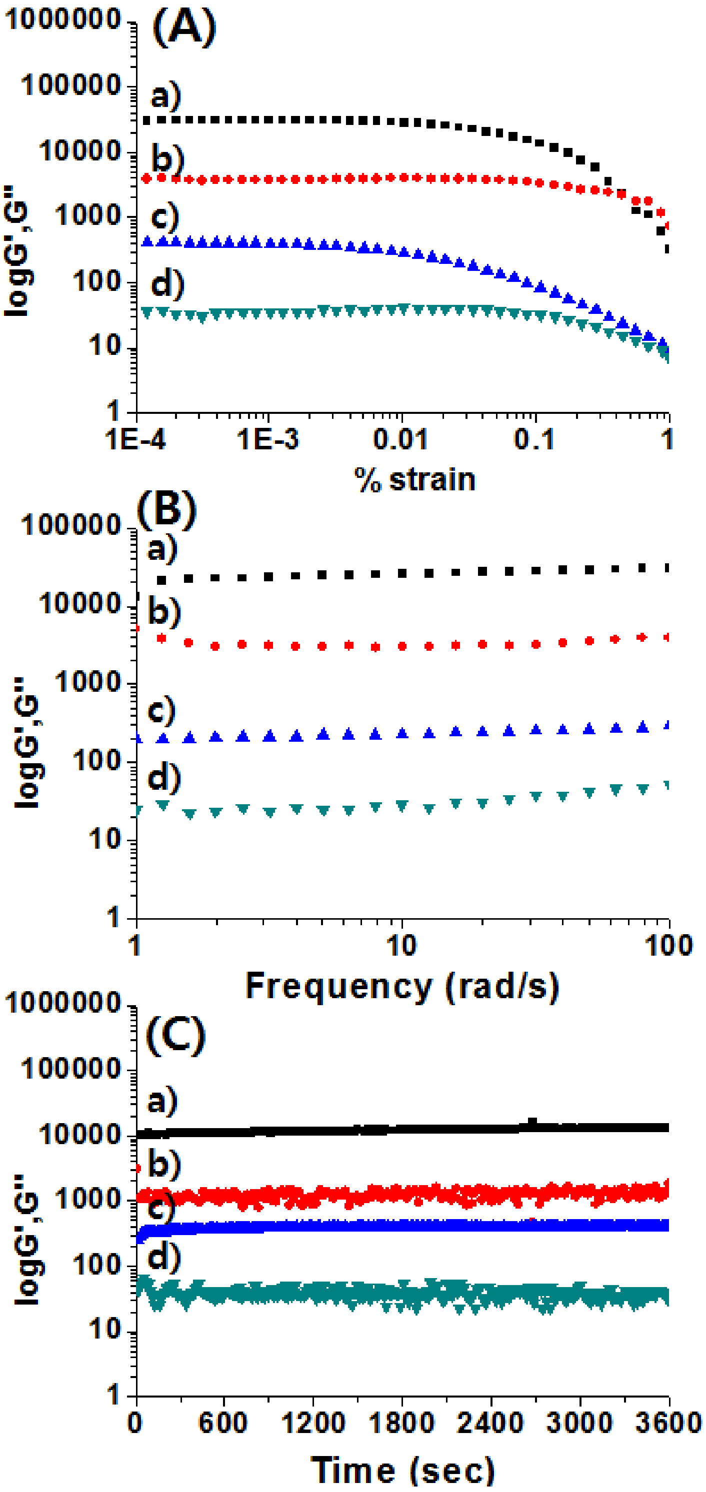

Fig. S10 Rheological measurement of (A) Strain sweep at a frequency 1 rads^{-1}, (B) Freequency sweep at a strain 0.01%, (C) Time sweep at a Freequency 1 rads^{-1} and a strain 0.01% of hydrogels **1**; (a) G' and (b) G'' and **2**; (c) G' and (d) G''.