

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for

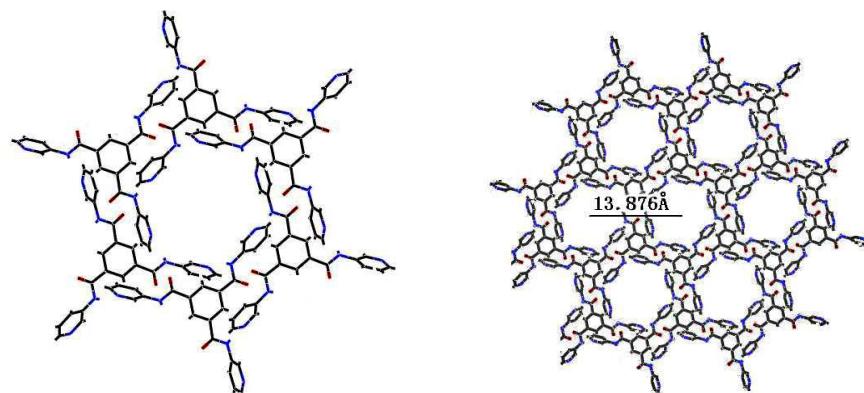
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Supporting Information

A smart supramolecular hydrogel: pH-modulated reversibly viscoelastic properties

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(a) The proposed assembly

(b) The 2-Dimensional extended assembly of (a)

Figure S1. The proposed assembly mode in the hydrogel of the pure amide. [1]

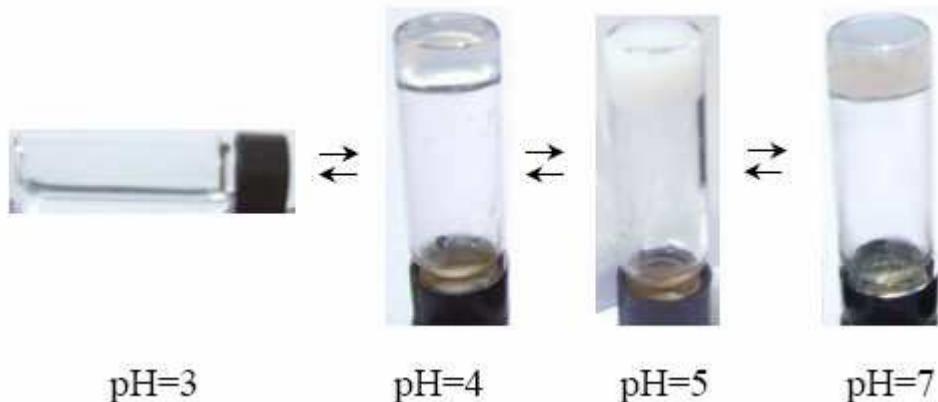


Figure S2. Corresponding images of the gel at different pH values captured by a digital camera.

Table S1. The states of the gel at different pH values in EtOH/H₂O mixtures (0.55 wt %, 1:1 v/v).

pH<3	pH=3–4	pH=4–6	pH=6–7
sol	transitional state	rigid gel	less rigid gel

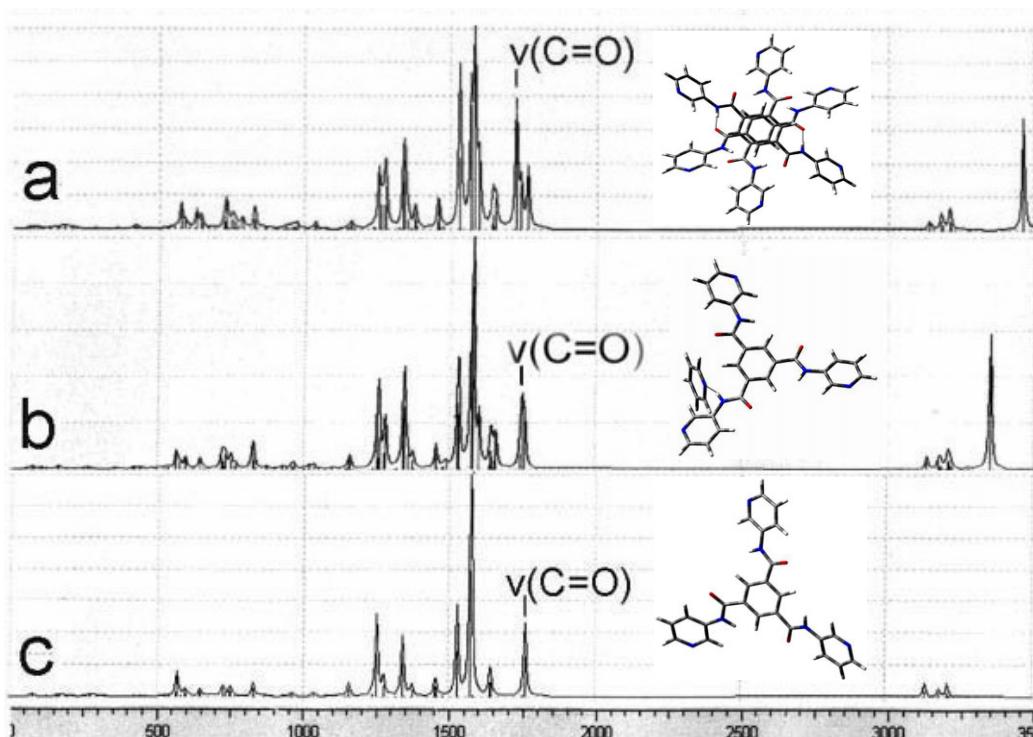


Figure S3. The energy-optimized model structure and the corresponding calculated FT-IR spectra of (a) Model I: two amide molecules form strong hydrogen bonds of C=O...H-N, $\nu(\text{C}=\text{O})^{\#}$: **1653-1657 cm⁻¹** (corresponding to the hydrogen bonded amide C=O group, $d_{(\text{N}-\text{H} \dots \text{O})}=3.01 \text{ \AA}$). (b) Model II: one pyridine molecule hydrogen-bonded to N-H group of one amide, $\nu(\text{C}=\text{O})$: **1678-1683 cm⁻¹**, $d_{(\text{N}-\text{H} \dots \text{NPy})}=3.07 \text{ \AA}$. (c) Model III: an isolated amide, $\nu(\text{C}=\text{O})$: **1691-1694 cm⁻¹**. All the related hydrogen bonds are indexed by black line. “● ● ●” denote C, H, N, O atom respectively. [#] Based on B3LYP/6-31G** method ^[2], the calculated vibration frequency should time a factor of 0.9614 before using. **These model systems are designed only for simulation, and it doesn't mean they exist in reality.**

Table S2. Differences in FT-IR spectra by Figure 4II and 4III.

cm ⁻¹	v (N-H)	Amide I v (C=O)	Amide II δ (N-H)	2000-2600
Powder B (Figure 4II)	3443 , 3255	1696 , 1682	1542	2122, 2552
[AH ₃] ³⁺	3414	1693	1549	2030, 2557
Powder A (Figure 4III)	3276	1682, 1657	1535	none
Powder A -180 °C	3263	1682, 1650	1532	none

The definition of origins of the observed C=O stretching bands:

In FT-IR spectrum of Powder A, the stretching vibration band of the amide N-H group located at ~3260 cm⁻¹ indicates that the N-H group of the amide molecule is involved in intermolecular hydrogen bonds ^[3] (Figure 4III). It is possible that N-H group of an amide is hydrogen-bonded to the C=O group (N-H…O=C) or the pyridyl nitrogen of its nearby molecule (N-H…Py).

Now we will give a tentative analysis on the origins of the observed C=O stretching bands, which is of great value for elucidating the hydrogen bonding. For this purpose, theoretical calculations have been performed on three model systems. Model I is an assembly of two amide molecules, in which the C=O group of one amide is hydrogen-bonded to the N-H group of another (Fig. S3-a). The optimized structure shows two strong N-H…O=C hydrogen bonds ($d_{N-H \cdots O} = 2.0 \text{ \AA}$). The calculated C=O stretching band is at 1653 cm⁻¹. This result indicates that the intermolecular N-H…O=C hydrogen bond may be responsible for the observed band of 1650 cm⁻¹. In Model II, one pyridine molecule is hydrogen-bonded to the N-H group of one amide. Stretching band of C=O is calculated to be at 1678 cm⁻¹, which is close to the observed band 1682 cm⁻¹ (Fig. S3-b, N-H…Py). Additionally, the amide I band in an isolated amide (Model III) is calculated to locate at 1694 cm⁻¹ (Fig. S3-c). This value is in good agreement with the 1696 cm⁻¹ band appearing in the FT-IR spectra of Powder B. Thus, a comparison of our calculated C=O stretching frequencies with experimental IR spectra indicates distinct hydrogen bonding interactions in these samples.

In conclusion, the amide I band in free C=O group of amide appears at ~1694 cm⁻¹,

hydrogen bonding induces red-shift to 1682 cm⁻¹ (N-H…Py), 1675 cm⁻¹ (solvent…O=C-N-H…Py, solvent of hydrogel), 1657 cm⁻¹ (C=O…solvent) and 1650 cm⁻¹ (N-H…O=C), respectively.

In Powder A, there have two kinds of hydrogen bonding, which make the amide I band split into two peaks at 1682 cm⁻¹ (N-H…Py) and 1657 cm⁻¹ (C=O…solvent), while at 1682 cm⁻¹ and 1650 cm⁻¹ (N-H…O=C) in the sample dried in vacuum at 180 °C, because removing solvent molecules is of benefit to form N-H…O=C hydrogen bonds (Figure 4III).

Due to the presence of protons, pyridyl groups are partially protonated in Powder B or completely protonated in [AH₃]³⁺, then the hydrogen bonds of N-H…Py are broken partially or completely. Therefore, there exist two amide I bands at 1696 cm⁻¹ (free C=O group) and 1682 cm⁻¹ (N-H…Py) for Powder B and one band at 1693 cm⁻¹ for [AH₃]³⁺ (Figure 4II).

Additionally, the ν -NH bands of 3200-3300 cm⁻¹ are indicators of hydrogen bonded N-H group, while the band centered at ~3400 cm⁻¹ indicates no obvious amide aggregation or the hydrogen bonds are broken. Combined with amide I bands, the existence of **both** the two ν -NH bands at 3443 cm⁻¹ and 3255 cm⁻¹ in Powder B further evidenced hydrogen bonds of N-H…Py are partially broken (Figure 4II-a and Table S2), while **single** ν -NH band at 3414 cm⁻¹ indicates hydrogen bonds of N-H…Py are broken completely in [AH₃]³⁺ (Figure 4II-b and Table S2). This confirmed our attribution about these amide I bands.

References

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