New Hydrogen-bonded Supramolecular Hydrogels and Fibers Derived from 1,2,4,5-Benzenetetracarboxylic Acid and 4-Hydroxypyridine

Yujiang Wang, Liming Tang,* and Yan Wang
Advanced Materials Laboratory, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China

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A new kind of supramolecular building unit was synthesized from 1,2,4,5-benzenetetracarboxylic acid and 4-hydroxypyridine by a simple procedure. The structure of the building unit was characterized by ^{1}H NMR spectroscopy, IR spectroscopy, EA, and XRD. Under suitable conditions, supramolecular hydrogels and fibers were formed from the building unit through hydrogen bonds between the donors and acceptors.

Supramolecular polymers[1–3] linked by hydrogen bonds of the building units have gained great interest since the pioneer work from 1997.[4,5] These polymers have demonstrated properties similar to covalent-bonded polymers but with much stronger temperature dependent characters. In some cases, supramolecular polymers are formed from different building units with each carrying one kind of functional groups. The supramolecular structures and properties are obviously affected by the stoichiometric ratio and the miscibility of the building units. Some studies also concerned about building units bearing both donor and acceptor groups. However, the difficulties in their synthesis have become a great challenge for practical uses. Recently, supramolecular gels formed from small organic molecules in organic solvents or water have become a rapid expanding research area due to their potential applications,[6–10] such as sensitive materials that reversibly respond to various external stimuli.[11,12] However, it is still a difficult task to form gels in water (also termed as hydrogels) mainly based on hydrogen bonds because some of the bonds can be disrupted by water molecules.

In the present study, we found that a new building unit synthesized from 1,2,4,5-benzenetetracarboxylic acid and 4-hydroxypyridine was able to form supramolecular hydrogels and fibers based on the hydrogen bonds of the molecules. The supramolecular performances with respect to temperature were investigated.

Firstly, at molar ratio of 1:2, 1,2,4,5-benzenetetracarboxylic acid and 4-hydroxypyridine were dissolved in DMSO in a flask equipped with a magnetic stirrer and a condenser. After elevated to 90 °C, the solution was stirred at this temperature for 2 h. The solution was precipitated into chloroform. After filtration, the crude product was washed by ethanol and acetone with each for three times. After dried to a constant weight in an oven, a grey powder-like product was obtained in rather high yield (86%) with a melting point of 234–236 °C. ^{1}H NMR (D$_2$O, 25 °C, 500 MHz, ppm): δ 6.99–7.00 (4H, pyridyl H-3), 7.88 (2H, Ar–H), 8.16–8.18 (4H, pyridyl H-2). The existence of only three peaks and their accurate integral ratio of 2:4:4 indicated that the building unit has a symmetrical structure formed at a stoichiometric ratio of 1:2 of the two reactants. IR (KBr, γ, cm^{-1}): 1890 (characteristic peak of hydrogen bond formed between pyridyl and carboxylic groups),[13] 1645 (C=O, blue shift compared with that of tetracarboxylic acid), 3093 (carboxylic –OH, red shift compared with that of tetracarboxylic acid). The IR results indicated that hydrogen bonds between pyridyl and carboxyl groups are formed in the building unit.[14] EA: found: C, 53.93; H, 3.54; N, 6.26%. calcd for $C_{20}H_{16}N_2O_{10}$ according to the building unit shown afterwards: C, 54.05; H, 3.60; N, 6.31%.

To get an insight of the structure of the building unit, a model compound was prepared from 4-hydroxypyridine and *o*-phthalic acid by the same method. The single crystal of the compound obtained by slow crystallizing in water was measured by Bruker P4 Diffractometer equipped with graphite monochromatized Mo Kα radiation at room temperature (21 ± 1 °C). From the results in Figure 1 and Table 1, it is noticed that both of the carboxylic acid groups in *o*-phthalic acid form hydrogen bonds with pyridine group of 4-hydroxypyridine. In addition, new hydrogen bond formed from two phenolic hydroxy groups after transferring one proton further facilitates the formation of the single crystal. The crystal structure of the model compound can be used to explain the connecting fashion of the building unit.

Figure 2 shows the powder X-ray diffraction diagrams (XRD) of 1,2,4,5-benzenetetracarboxylic acid, 4-hydroxypyridine, and their building unit measured at room temperature. For the building unit, the onset diffraction is located at 8.38° (2θ) corresponding to a d spacing of 10.69 Å. In connecting with the other differences in diffraction signs between the building unit and the two reactants, it is assumed that a new crystal structure had been formed.[15] Considering the structure of the model compound, it is reasonable that such a length is close to the total molecular length of the two reactants. Based on all these measurements, the structure of the building unit can be defined in Figure 2, in which two 4-hydroxypyridine units are hydrogen bonded to 1,2,4,5-benzenetetracarboxylic acid unit based on the recognizing sites from the same side.

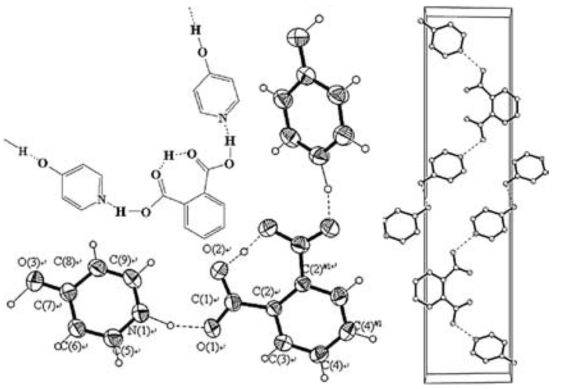

Figure 1. Crystal structure and packing view along the *a* direction of the model compound derived from 4-hydroxypyridine and *o*-phthalic acid.

Table 1. Summary of crystallographic data of the model compound

Molecular formula: $[C_6H_4(COOH)_2][C_5H_4NOH]_2$
Molecular weight: 356.33
Color and habit: dark brown prism Crystal size: $0.1 \times 0.1 \times 0.4\,mm^3$
Crystal system: monoclinic
Space group: $P2_1/m$
Unit cell parameters: $a = 4.0010(4)$ Å, $\alpha = 90.00°$
$b = 29.881(5)$ Å, $\beta = 93.815(11)°$
$c = 6.8747(10)$ Å, $\gamma = 90.00°$
$V = 820.1(2)$ Å^3 $Z = 2$ $F(000) = 372$
Density (calcd): $1.443\,g/cm^3$

$R1$	0.1504	0.0541
$wR2$	0.1511	0.1052

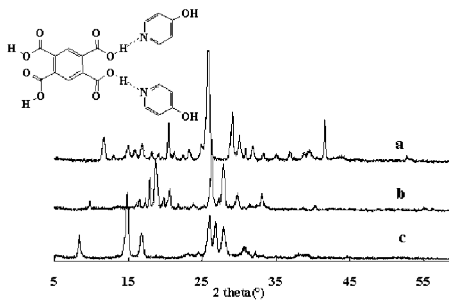

Figure 2. X-ray diffraction diagrams for (a) 1,2,4,5-benzenetetracarboxylic acid, (b) 4-hydroxypyridine, and (c) the building unit.

The presence of different kinds of functional groups makes the building unit possible for supramolecular assembling. Firstly, supramolecular hydrogel of the building unit was formed by the following procedure. 0.05-g building unit was added into 2-mL distilled water in a test tube to form a grey-like suspension. After heated at 90 °C, the suspension gradually turned to a red transparent solution. Then, the tube was taken out and cooled to 25 °C at a cooling rate of 10 °C/min. During this course, a grey supramolecular hydrogel was formed spontaneously and the gel kept stable during hand shaking. However, the hydrogel collapsed into flowing state if the temperature was elevated to a certain point. The sol–gel transition phenomenon can be repeated for many times as the change of temperature.

To see further details of the gel, SEM analysis of the xerogel was performed by JSM-6301F scanning electron microscope. From the results in Figure 3, it reveals that xerogel is composed of intertwined flexible fibrous network. The length is higher than 100 μm and the width is from 200 to 500 nm for the fibers. It is generally acknowledged that the flexible fibers became entangled and formed networks, which trapped water molecules via surface tension.[6,11] The network structure of the xerogel was also observed even under an optical microscope. It is assumed that the macroscopic flexible fibers present in the gel were constructed from the building unit. To our knowledge, such large fibers formed through hydrogen bonds in water have seldom been reported in the literature.[12]

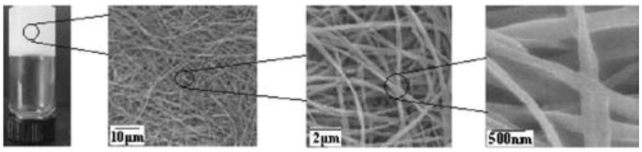

Figure 3. SEM images of the xerogel from the hydrogel (25 $mg{\cdot}mL^{-1}$).

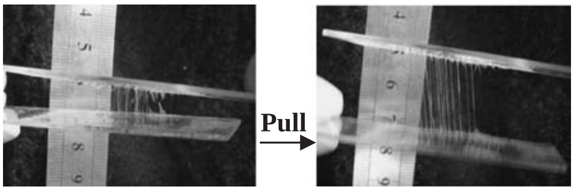

Figure 4. Fibers formed from the melting building unit.

Furthermore, small amount of the building unit was placed between two glass slides and heated to melting state. At temperature slightly lower than the melting point, the slides were quickly pulled aside by hands. From Figure 4, supramolecular fibers of several centimeters were noticed between the slides, indicating strong interaction of the molecules. The fiber length is greatly affected by the temperature. Once the building unit became solid at even lower temperature, no fiber could be formed any more.

The above results suggested that the building unit can form supramolecular structures with properties similar to ordinary polymers at conditions where hydrogen bonds are favorably formed.[16] Based on crystal structure of the model compound, it is assured that the building units connected with each other at least through hydrogen bonds are formed from phenolic hydroxy groups. Although it is still not clear how carboxylic acid groups play role in the molecular connection, these polar groups are thought to absorb water molecules into the networks. In summary, we described here a new building unit, which can be synthesized by quite simple procedure. The formation of supramolecular hydrogels and fibers at suitable conditions should make it possible for various uses.

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