Journal of Molecular Liquids 180 (2013) 129–134

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Highly directional co-assembly of 2,6-pyridinedicarboxylic acid and 4-hydroxypyridine based on low molecular weight gelators

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ARTICLE INFO

Article history:
Received 6 April 2012
Received in revised form 9 January 2013
Accepted 9 January 2013
Available online 4 February 2013

Keywords:
Two component gelator
Co-assemble
Directional interaction
Hydrogen bonding
π–π stacking

ABSTRACT

The highly directional interactions among complex gelators of 2,6-pyridinedicarboxylic acid and 4-hydroxypyridine are investigated, which lead to the formation of ordered one-dimensional fibers with diameters of 500 nm~2 μm. By scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, and X-ray powder diffraction (XRD), the co-assembly of the complex into straight fibers under the function of multiple directional hydrogen bonds and π–π stackings is proved. The strong and directional interactions lead to rich dynamic behavior and high degrees of internal order among the complex gelators. The ordered one-dimensional co-assemblies possess useful functions in templated synthesis, molecular recognition, enzyme immobilization, and other biochemistry fields.

1. Introduction

Supramolecular functional hydrogels constructed through self-assembly of low molecular weight gelators (LMWGs) intermediate between liquids and solids, and possess several intriguing solid-like properties [1]. They can self-assemble into functional materials displaying a hierarchy of structure over several length scales. Unlike in covalently connected polymers or inorganic hydrogels [2–4], LMWGs are held together by non-covalent interactions (e.g. hydrogen bonding, π–π stacking, hydrophobic, and van der Waals interactions) to form hydrogel matrix [5]. Therefore, subtle changes applied to LMWG system via external stimuli like pH changes, light, temperature and chemicals may already trigger the gel-to-sol transition of LMWGs. By using this attractive feature, supramolecular hydrogels have diverse applications, being widely used in tissue engineering [6], drug delivery [7], separation technology [8], templated synthesis [9], and so forth.

So far, a wide range of LMWGs have been found including elongated hydrocarbons [10], aromatic molecules [11], saccharides [12], amino acid based systems [13], and some others. In most of examples, the low molecular weight hydrogels are one component gels, but recently interest in two component gels has increased [14,15]. In two component gels, an initial interaction occurs between the two components to form a complex, which subsequently co-assembles into a fibrous supramolecular network structure. Compared with single component gels, two component gels offer the potential of developing more soft materials with highly tunable microscopic and macroscopic properties [16,17]. Firstly, the formation of the complex prior to fibrillar assembly offers an additional level to control in the hierarchical self-assembly process, and indeed this level of control is difficult to replicate in one component gelation systems. Secondly, in two component hydrogels, it is easy to introduce functional behavior into the materials through modifications of either one of the two components. Finally, the morphologies and properties of two component hydrogels can be intricately tuned by varying the ratio of the two components.

To date, two component gelators consisting of L-lysine derivatives and aliphatic acids [18], maleic N-monoalkylamides and aliphatic amines [19], aliphatic amines and carbon dioxide [20], Au-pyrazolate and C_{18} alkyl chains [21] have been reported, providing ample evidence of the promising features of the two component approach to achieve gel. However, most of these two component gelators are absence of enough directional interactions, which cannot provide ordered and straight fibers with lengths of hundreds of micrometers. This makes it difficult to control the morphology of co-assembly.

To further enrich the knowledge base of two component hydrogel system with desired ordered fibers, herein, we report a new class of two component gelators comprised of 2,6-pyridinedicarboxylic acid and 4-hydroxypyridine. Due to the multiple directional hydrogen bonds and π–π stackings, the complex can aggregate to produce the ordered and straight fibril and hence gel formation. The use of strong and directional interactions among the complex gelators can efficiently improve order of co-assemblies. Their gelation ability, microstructures, and interactions between the components were explored and characterized.

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http://dx.doi.org/10.1016/j.molliq.2013.01.005

2. Experimental

2.1. Materials and synthesis

All starting materials were purchased from Aladdin and used without further purification. The complex gelator (complex G) (Scheme 1) was synthesized according to the procedure described as follows: a mixture of 2,6-pyridinedicarboxylic acid (3.34 g, 20 mmol) and 4-hydroxypyridine (4.18 g, 44 mmol) in 50 ml DMSO was stirred at 100 °C for 3.5 h. Subsequently, 200 ml chloroform was added and the white precipitate that formed was collected by filtration, and washed with ethanol and acetone, respectively. Drying of the remaining white solid in vacuum gave pure complex G. Yield: 59.8%.

Complex G: ^{1}H NMR (400 MHz, DMSO-d6, δ): δ = 6.22 (d, 4H, pyridyl H-2), 7.72 (d, 4H, pyridyl H-3), 8.14–8.25 (q, 3H, pyridyl H-3, H-4) ppm.

2.2. Gelation test

The required amounts of complex G were slowly heated to dissolve in water and then were allowed to cool slowly to room temperature. After 10–15 min the solid aggregates were stable to inversion of the glass vial, and the complex G was recognized to form gels.

2.3. Determination of the gel-to-sol transition temperature (T_{gs})

All the gel-to-sol transition temperatures (T_{gs}) were determined using the "dropping ball" method [22], which consisted of carefully placing a stainless steel ball (0.5 g, 4 mm in diameter) on top of a gel that had been prepared in 3 ml glass vials, and subsequently placing these vials in a thermostated oil bath. The temperature of the heating block was increased by 10 °C per minute and the T_{gs} was defined as the temperature at which the stainless steel ball reached the bottom of the vial.

2.4. Microscopy study

Scanning electron microscopy (SEM) images were obtained on a FEI QUANTA 250 microscope. A drop of gel (at 0.1%, 0.5%, 3%, respectively) was placed on a silicon slice and dried under vacuum before imaging.

2.5. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra of 2,6-pyridinedicarboxylic acid, 4-hydroxypyridine, and complex G were taken using a Bruker EQUINOX55 instrument. The KBr disk technique was used for the solid-state measurement. The samples were then scanned between the wavelengths of 4000 and 400 cm^{-1} at an interval of 1.9285 cm^{-1}.

2.6. ^{1}H nuclear magnetic resonance (^{1}H NMR) experiments

^{1}H NMR studies were carried out on a Bruker Advance III 400 instrument operating at 400 MHz. The spectra of 4-hydroxypyridine and complex G were recorded in DMSO.

2.7. Ultraviolet–visible (UV–vis) spectroscopy

UV–vis absorptions were recorded on a Tecan Infinite 200 Pro spectrometer. To study the effect of hydrogen bonding on the structure of complex G, 2,6-pyridinedicarboxylic acid, 4-hydroxypyridine, and complex G at 1×10^{-4} mM were prepared. Data were collected between the wavelengths of 230 nm and 360 nm with bandwidth of 1 nm.

2.8. X-ray powder diffraction (XRD)

The complex G hydrogel was filtered and dried under vacuum to obtain the xerogel. The XRD pattern was recorded on an Anton Paar SAXSess instrument.

2.9. Elemental analysis

Elemental analysis was performed on a model Vario-ELIII IRMS elemental analyser. The elemental analysis results for the 2,6-pyridinedicarboxylic acid, 4-hydroxypyridine, and complex G are as follows: elemental anal. Calcd. for $C_7H_5NO_4$ (mol.wt.: 167.1): C, 50.3%; N, 8.4%; Found: C, 50.4%; N, 8.6%. Calcd. for C_5H_5NO (mol.wt.: 95.1): C, 63.2%; N, 14.3%; Found: C, 63.2%; N, 14.7%. Calcd. for $C_{17}H_{15}N_3O_6$ (mol.wt.: 357.3): C, 57.1%, N, 11.8%; Found: C, 58.7%; N, 12.4%.

3. Results and discussion

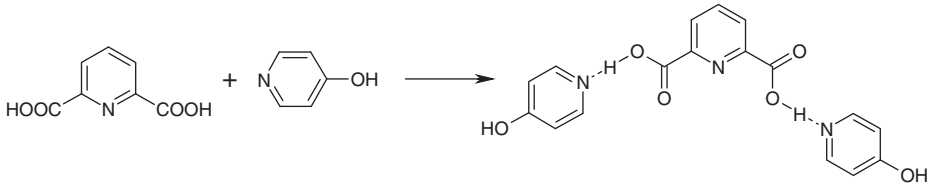
3.1. Gelation test

In Scheme 1, molecular structure of 2,6-pyridinedicarboxylic acid, 4-hydroxypyridine, and complex G is presented. According to the ^{1}H NMR and elemental analysis, the complex G was determined to form at 2,6-pyridinedicarboxylic acid/4-hydroxypyridine of 1:2. It was found that single component 4-hydroxypyridine formed a solution, and 2,6-pyridinedicarboxylic formed a precipitate (Fig. 1a). However, the complex G expressed excellent gelation properties, with gelation concentration at 5 wt.% (Fig. 1b).

Complex G is a thermoreversible hydrogelator. The complex G in water was slowly heated until it turned into a clear solution, then an immobilized hydrogel was observed when the solution was cooled down to room temperature. This gelation process can be repeated many times. The lowest concentration of gelator was 2.5 wt.% for complex G. The thermoreversible gel-to-sol phase transition can conveniently be characterized by determining the temperature at which the gels turn into solutions (T_{gs}). Fig. 2 clearly shows that increasing the concentration of complex G leads to higher T_{gs} values. The stability of gel is sharply enhanced immediately following the increase of concentration of the gelator. When the concentration reaches 5.41%, the increase of T_{gs} slows down. The T_{gs} reaches a value of 86 °C at 9.91 wt.% for complex G, indicating the high stability of the gel. Hence, the formation of gel-structure is essentially complete at a higher complex G concentration region.

3.2. Characterization of complex G hydrogel

In order to gain an insight into the aggregate morphology of complex G hydrogel, hydrogels of different concentrations were studied



Scheme 1. Preparation of the complex G.