COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Inter- and intra-molecular H-bonds induced different nanostructures from a multi-H-bonding (MHB) amphiphile: nanofibers and nanodisks†

Peng Gao,[ab] Chuanlang Zhan,*[a] Lizhu Liu,[b] Yanbiao Zhou[a] and Minghua Liu*[a]

[a] *CAS Key Laboratory of Colloid and Interface Science, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, P.R. China. E-mail: liumh@iccas.ac.cn; Fax: 86-10-62569564; Tel: 86-10-82615803*

[b] *College of Material Science and Engineering, Harbin University of Science and Technology, Heilongjiang 150080, P.R. China*

Received (in Cambridge, UK) 27th February 2004, Accepted 18th March 2004
First published as an Advance Article on the web 27th April 2004

An MHB amphiphile, *N*-stearoyl-L-glutamic acid (C_{18}-Glu), forms disk- and fiber-like nanostructures respectively in hydrophilic and hydrophobic environments due to the inter- and intra-molecular H-bonds.

Self-assembly of low molecular-mass gelators (LOMGs) held together by noncovalent intermolecular interactions have recently received much more attention because of their interesting morphologies and potential applications in the fields of template synthesis and functional materials.[1–3] One of the basic studies in this field is to control the morphology and property of the self-assembled nanostructures. It is reported that such control could be achieved by changing gelating conditions such as the concentration of LOMG[4] and the pH value of the envirnoments[5] as well as the molar ratio of **A** to **B** for dual-component organogels.[6] For example, carboxylic acid–based LOMGs would result in a very different nanostructure after neutralization.[5] Herein, we report an experimental observation for the morphological changes of organogels through changing of the inter- or intra-molecular H-bonds *via* hydrophilic or hydrophobic environments of the solvents. The investigated LMOG was C_{18}-Glu, which has two carboxylic acids and one amide group and can therefore provide MHB sites.

C_{18}-Glu was synthesized from the amidation of diethyl L-glutamic ester hydrochloride (Acros) with stearic acid (Acros) and subsequent hydrolysis in a dilute NaOH methanol solution. The gelating tests indicated that C_{18}-Glu could form white organogels with each of chloroform (gel **I**) and 1:1 mixed water/ethanol (V/V) (gel **II**). About 16 and 20 mg of C_{18}-Glu were necessary to harden 1 ml of the 1:1 mixed water/ethanol and chloroform gels, respectively. Precipitates were formed in solvents such as petroleum ether, hexane, ethyl ester, acetone and water.

The self-assembled nanostructures of gels **I** and **II** were investigated with tapping mode Atomic Force Microscopy (AFM) and Scanning Electronic Microscopy (SEM). Fig. 1 shows the SEM and AFM height images of xerogels **I** (a) and **II** (b), respectively. C_{18}-Glu formed into ribbon-like microstructures (Fig. 1a) in chloroform. Each of the ribbons was observed to be constructed from several nanofibers with diameters of *ca.* 30–80 nm (inset in Fig. 1a) and lengths up to tens of microns. However, in the gel **II**, C_{18}-Glu formed into nanodisks. The diameters of the nanodisks are of tens to hundreds of nanometers. An enlargement (inset in Fig. 1b) reveals that some of the nanodisks were constructed by two or three layers with one above the other. The height of one layer was estimated to be *ca.* 3.2 nm. XRD patterns of both the organogels revealed that the *d*-spacing of the nanodisks was *ca.* 3.2 nm, and that of nanofibers was *ca.*3.4 nm. The two *d*-values were all larger than one molecular length of C_{18}-Glu and smaller than twice the molecular legngth. This indicated that a molecular bilayered structure with the alkyl chain interdigited by the hydrophobic interactions was formed in both the solvents.

As reported in the literature, C_{18}-Glu molecules can form intermolecular chiral H-bonds between –NH and –CO in –COOH in hydrophilic surroundings such as ethanol, methanol, and water/alcohol.[7,8] In the case of **II**, the C_{18}-Glu molecules also tend to form

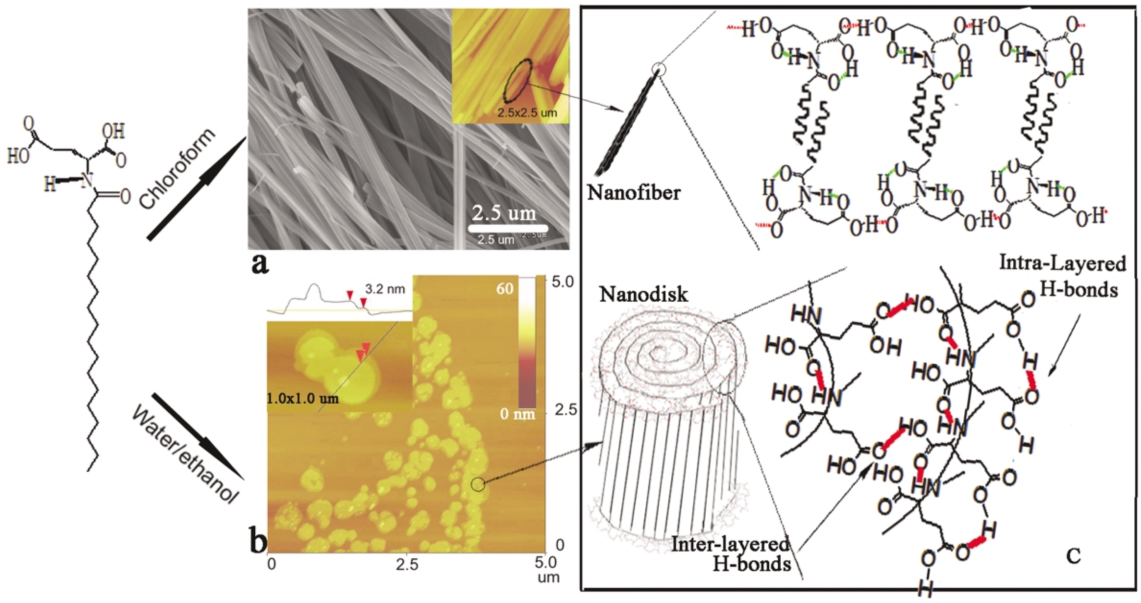

Fig. 1 AFM and SEM images of xerogels **I** (a) and **II** (b). (c) Possible models of the self-assembly of C_{18}-Glu into nanofibers in chloroform and nanodisks in 1:1 mixed ethanol/water with green and red lines representing the intra- and inter-molecular H-bonds, respectively.

---

† Electronic supplementary information (ESI) available: experimental data, AFM, SEM images, XRD, FT-IR and CD spectra of gels **I** and **II**, and molecular models. See http://www.rsc.org/suppdata/cc/b4/b402956a/

DOI: 10.1039/b402956a

This journal is © The Royal Society of Chemistry 2004

this kind of chiral H-bond in the cooling process. This is supported by the FT-IR spectra of the xerogel **II**. The amide-**II** band at 1552 cm^{-1} suggests that the NH group forms H-bonds, confirmed by the red-shift of ν_{NH} to 3310 cm^{-1}, whereas the strong amide-**I** band, occurring at 1650 cm^{-1}, indicates that the CO group is free of H-bonds. The broad band of $\nu_{C=O}$ with two peaks at 1745 and 1717 cm^{-1} indicates the existence of free, laterally H-bonded and bifurcated –COOH groups,[9] being possible for formation of the intra- and inter-layered H-bonds between intermolecular –COOH and/or amide groups. The FT-IR spectrum of gel **I** is very different from that of gel **II**. The amide-**I** and -**II** bands appear at 1643 and 1541 cm^{-1}, respectively, suggesting that both the CO- and NH-groups all form H-bonds. The $\nu_{C=O}$ bands at 1727 and 1683 cm^{-1}, respectively, indicate that the –COOH groups simultaneously form lateral inter- and intra-molecular H-bonds, which is supported by the broad, strong vibration band at 3500–2800 cm^{-1} with a peak at 3060 cm^{-1}. The FT-IR data suggest that C_{18}-Glu forms inter-molecular H-bonds in 1:1 mixed ethanol/water, whereas it forms intra- and inter-molecular H-bonds in chloroform. This is further comfirmed by temperature-dependent ^{1}H-NMR spectra.

As shown in Fig. 2, there is a slight downfield shift of the proton of the amide upon heating each of the gels in $CDCl_3$. This clearly reveals the formation of H-bonds for the –NH units in the gels.[10] Significant differences are observed for the protons of –COOH in the two gels. At a lower temperature of 325 K, a broad peak ascribed to the protons of –COOH was observed at *ca.* 3–7 and *ca.* 1–4 ppm, repestively, for gels **I** and **II**, suggesting H-bonding of –COOH in the gels, which is further supported by the following downfield shift upon heating. However, the shifted pattern was very different. In the gel **I**, only one broad peak corresponding to two protons was observed at each temperature, suggesting that the two protons of –COOH have similar environments in gel **I**. On the other hand, in gel **II**, three peaks were observed at 6.6, 7.2 and 9.3 ppm at 334 K, indicating that there are three different kinds of protons with different surroundings for –COOH in gel **II**. Moreover, the three peaks are relative to two protons. These strongly suggest that there exist two kinds of H-bonding protons and one kind of free proton for the two protons of carboxylic acid.

Based on the above results, models can be proposed to explain the formation of the different nanostructured organogels formed in the different solvents, as shown in Fig. 1c. In 1:1 mixed ethanol/water, the C_{18}-Glu molecules form intermolecular chiral H-bonds between the NH group of amide and the CO group of the –COOH unit which is directly linked to the chiral carbon atom,[7,8] and then assemble into a spiral molecular bilayer, *e.g.* one layered nanodisk. Moreover, part of the free –COOH groups can further form intra- and inter-layered intermolecular H-bonds between the adjacent –COOH groups in the spiral structure.[11] However, in chloroform, the intramolecular H-bonds were favored and the formation of both the intramolecular H-bonds between the amide and –COOH units[12] and then the intermolecular H-bonds between –COOH units would drive the C_{18}-Glu molecules to self-assemble into nanofibers through hydrophobic and hydrophilic interactions,[11] just as many reported fiber-mediated amphiphiles do.[1]

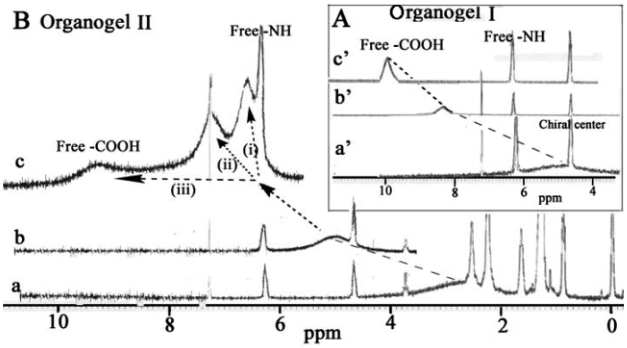

Fig. 2 ^{1}H-NMR spectra of gel **I** with $CDCl_3$ (a), and **II** suspended in $CDCl_3$ (b), respectively. a = a′ = 325 K; b = b′ = 330 K; c = c′ = 334 K.

In conclusion, the change from hydrophobic to hydrophilic surroundings depending on the solvents used would switch the intramolecular/intermolecular H-bonding styles and then control the morphology of the self-assembled nanostructures for C_{18}-Glu, an MHB amphiphile.

Authors would like to thank Professor Yalin Tang for his help in the NMR spectra. This work is supported by the NSFC (No. 20303024, 50172049, 90301010), the Major State Basic Research Development Program (No. G2000078103, 2002CCA03100).

Notes and references

1 J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263; P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133.

2 For examples of template synthesis, see: E. D. Sone, E. R. Zubarev and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2002, **41**, 1705; S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shinkai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550; C. Zhan, J. Wang, J. Yuan, H. Gong, Y. Liu and M. Liu, *Langmuir*, 2003, **19**, 9440.

3 For examples of functional materials, see: F. S. Schoonbeek, J. H. van Esch, B. Wagewijs, D. B. A. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellog and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393; F. Placin, J.-P. Desvergne and J.-C. Lassegues, *Chem. Mater.*, 2001, **13**, 117; A. Friggeri, O. Gronwald, K. J. C. van Bommel, S. Shinkai and D. N. Reinhoud, *J. Am. Chem. Soc.*, 2002, **124**, 10 754; A. Shumburo and M. C. Biewer, *Chem. Mater.*, 2002, **14**, 3745; M. George, S. L. Snyder, P. Terech, C. L. Glinka and R. G. Weiss, *J. Am. Chem. Soc.*, 2003, **125**, 10 275; K. Inoue, Y. Ono, Y. Kanekiyo, T. Ishi-I, K. Yoshihara and S. Shinkai, *J. Org. Chem.*, 1999, **64**, 2933.

4 J. H. Jung, S. Shinkai and T. Shimizu, *Nano Lett.*, 2002, **2**, 17.

5 J. Song, Q. Cheng, S. Kopta and R. C. Stevens, *J. Am. Chem. Soc.*, 2001, **123**, 3205.

6 A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts and A. C. Wright, *J. Am. Chem. Soc.*, 2003, **125**, 9010.

7 Y. J. Zhang, M. Jin, R. Lu, Y. L. Song, L. Jiang, Y. Y. Zhao and T. J. Li, *J. Phys. Chem. B*, 2002, **106**, 1960.

8 K. Sakamoto and M. Hatano, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 339.

9 M. Kogiso, T. Hanada, K. Yase and T. Shimizu, *Chem. Commun.*, 1998, 1791–1792; L. Sun, L. J. Kepley and R. M. Crooks, *Langmuir*, 1992, **8**, 2101; J. Dong, Y. Ozaki and K. Nakashima, *Macromolecules*, 1997, **30**, 1111.

10 M. Suzuki, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Chem. Eur. J.*, 2003, **9**, 348; F. H. Billiot, M. McCarroll, E. J. Billiot, J. K. Rugutt, K. Morris and I. M. Warner, *Langmuir*, 2002, **18**, 2993.

11 These models were supported by the CD sepctra of the xerogels **I** and **II** (ESI,† Fig. 5), the stronger CD signal of nanodisks indicates the formation of the intermolecular chiral H-bonds in the nanodisks.

12 Preliminary investigation by using PCMODEL minimizing indicates that the –COOH-to-amide intramolecular H-bonds are more stable than those between –COOH units in molecular energy (ESI,† Fig. 6).