Supplementary Material (ESI) for Chemical Communications

Supporting Information

Self-Assembled Helical Spherical-Nanotubes from an *L*-Glutamic Acid Based Bolaamphiphilic Low-Molecular-Mass Organogelator

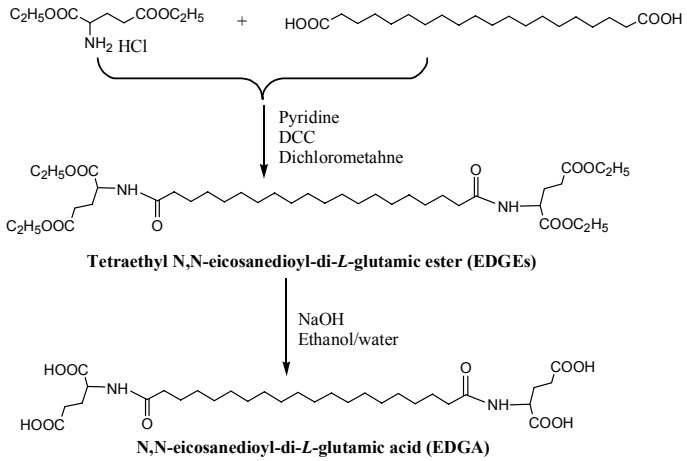
Chuanlang Zhan,Peng Gao, Minghua Liu[a,]*

CAS Key Laboratory of Colloid and Interface Science, Center for Molecular Science, Institute of Chemistry, CAS, Beijing 100080, P. R. China

1. EXPERIMENTAL

1.1 Synthesis

Eicosanedioic acid (TCI), and diethyl L-glutamic ester (Acros), and other chemicals were used as received. Deionized water was used.



Scheme 1. Synthetic routes of both **EDGA** and **EDGEs**.

Synthesis of EDGEs: 1.50g (6.3 mmol) diethyl ester of *L*-glutamic acid, 2.00 ml of pyridine, and 30 ml of toluene were mixed and stirred for 3 hrs. To which 1.10 g of (3.15 mmol) eicosanedioic acid, 3.00 g of dicyclohexylcarbodiimide (DCC), 0.30 g of 4-pyrrolidinopyridine were added. The resulted mixture was stirred overnight at 30° C. After removing the toluene, the white solid was recrystallized three times from a 1:1 mixed ethanol/water to give 1.20 g of **EDGEs** (yield 27%). ^{1}H-NMR (DMSO-d_6, δ, ppm): 1.28 (Strong s, 28H), 1.32 (t, 12H), 1.68 (t, 4H), 2.03 and 2.42 (two bands, m, 4H, attaching to chiral center), 2.23 (m, 8H), 4.13-4.27 (m, 8H), 4.64 (m, 2H, chiral center), 6.21 (d, 2H).

Synthesis of EDGA: 0.60 g (0.80 mmol) of **EDGEs**, 0.60 g of NaOH were added into 10 ml of 1:1 mixture of ethanol/water and stirred overnight at room temperature. The resulted solution was treated with 6N hydrochloric acid to bring pH = 1. The precipitated solid was filtered and then recrystallized from 100 ml of 1:1 mixture of ethanol/water to give 0.37 g of **EDGA** in a yield of 79%. ^{1}H-NMR (DMSO-d_6, δ, ppm): 1.23 (Strong s, 28H), 1.45 (t, 4H), 1.75 and1.93 (two bands, m, 4H, attaching to chiral center), 2.09 (m, 4H), 2.29 (m, 4H), 4.19 (m, 2H, chiral center), 8.03 (d, 2H). Elemental analysis: Calcd for $C_{30}H_{52}N_2O_{10}\cdot H_2O$: C (58.23), H (8.80), N (4.60); Found: C (58.43), H (8.63), N (4.62).

1.2 Formation of Organogels

A typical process for the preparation of organogel is as follows. **EDGA** was mixed in a sealed tube with a 1:1 mixture of ethanol/water at various concentrations, and the mixture was heated up to 70° C for several minutes to get a transparent solution. The sealed hot tube was then allowed to cool down to the room temperature unaffectedly. At a certain time, the organogels were formed. In order to characterize the organogel, freshly cleaved mica or copper grid or CaF_2 plates tied with a thread was put into the mixture of solvent and **EDGA** in the sealed tube and was then allowed to form organogel. The *in-situ* formed xerogels on the various substrates were used for various characterizations of AFM, FT-IR and TEM.

1.3 Instruments

AFM was performed using Tapping Mode (Nanoscope IIIa, Digital Instruments, Inc.) with a pyramidal Si_3N_4 tip. TEM was observed using a JEOL 300 system, which operates at 200 kV. FT-IR and UV-vis spectra were measured with a JASCO FT/IR-660 plus spectrometer and a JASCO 530 UV-vis spectrometer, respectively. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/Kα radiation (λ=1.5406Å), which was operated at 45 kV, 100 mA. ^{1}H-NMR spectra were recorded on a dmx 300 (Bruker) instrument. Elemental analysis was performed on a Carlo-Erba-1106 instrument.

Figure 1. AFM height and phase images (0.7 × 0.7 μm) of the helical spherical-nanotubes with an end.

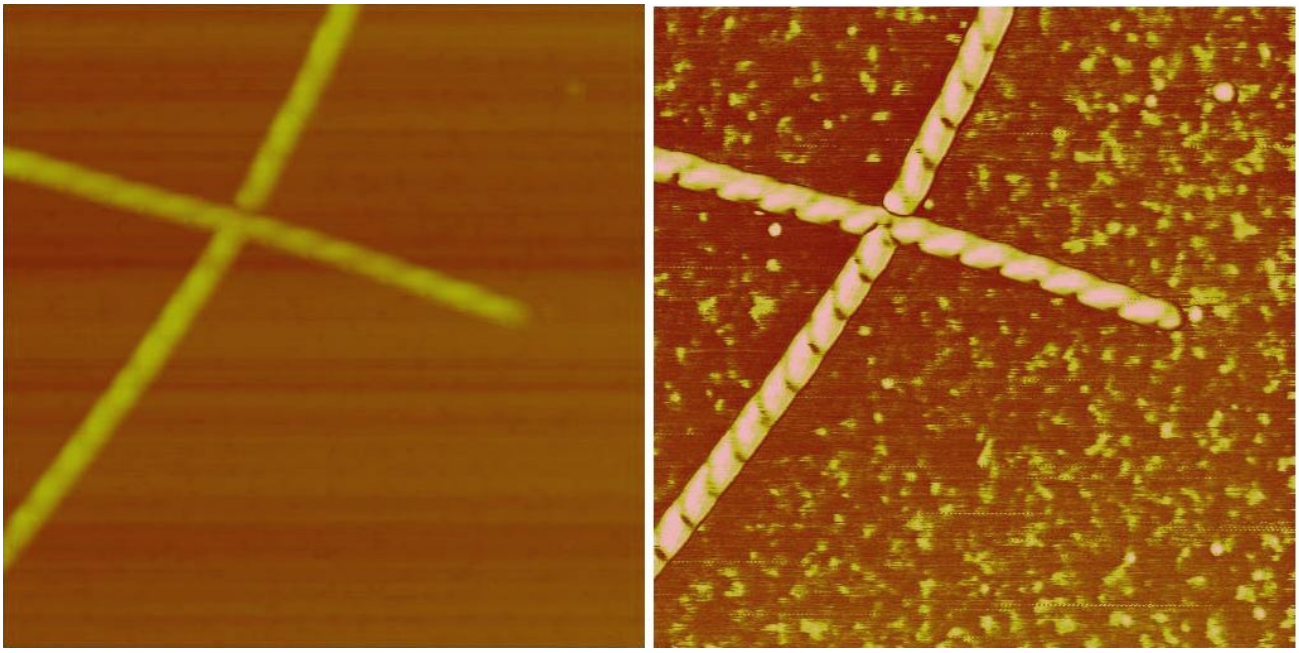


Figure 2. FT-IR spectrum of xerogels from **EDGA** and 1:1 mixture of ethanol/water with C_{gel} = 8.8 mM·L^{-1}.

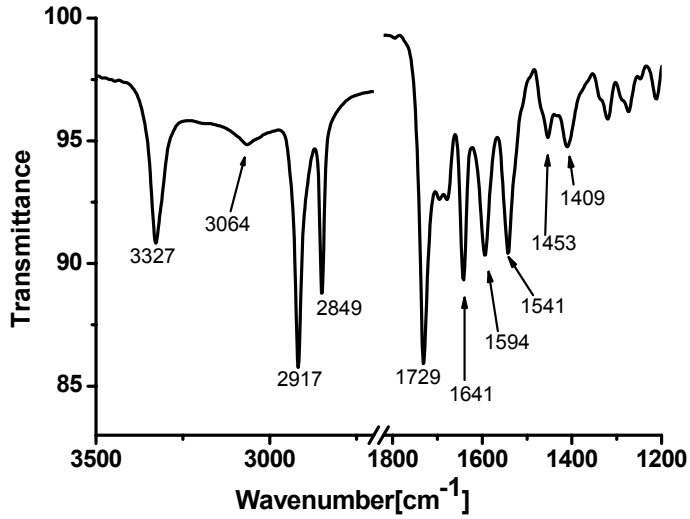


Figure 3. XRD patterns of xerogels from **EDGA** and 1:1 mixture of ethanol/water with C_{gel} = 8.8 mM·L^{-1}.

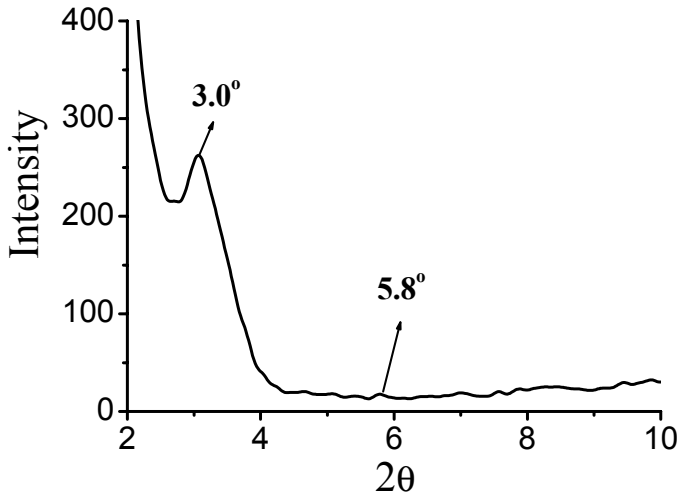


Figure 4. An AFM height image of self-assembled nanostructures from **EDGEs**.

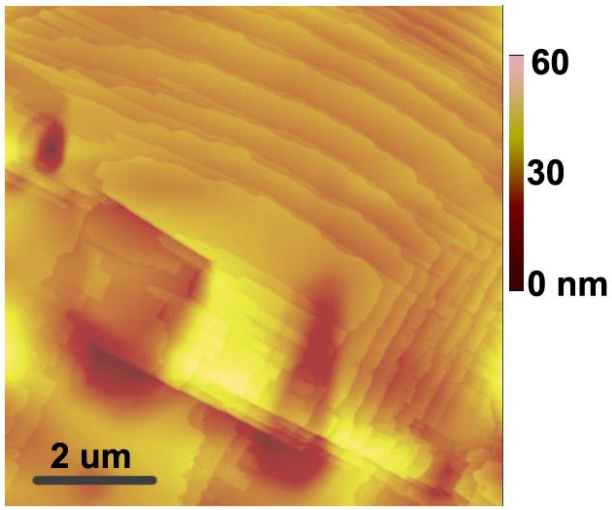


Figure 5. An AFM height image of self-assembled nanostrutures from monosodium salt of **EDGA**.