

Supporting information for

Copper (II) ion selective and strong acid-tolerable hydrogel by an L-histidine ester terminated bolaamphiphile: from single molecular thick nanofiber to single-wall nanotube

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Experimental Section

Instruments and methods: ¹H NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. Mass spectral data were obtained by using a BIFLEIII matrix-assisted laser desorption/ionization time-of flight mass spectrometry (MALDI-TOF MS) instrument. Elemental analysis was performed on a Carlo-Erba-1106 Thermo-Quest.

Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-660 plus spectrophotometer with a wavenumber resolution of 4 cm⁻¹ at room temperature. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/K α radiation ($\lambda=1.5406\text{\AA}$), which was operated at 45 kV, 100 mA. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 FE-SEM microscope and transmission electron microscopy (TEM) images were obtained on a JEM-1011 electron microscope operating at accelerating voltages of 10 and 200 kV, respectively.

Cryo-TEM was performed on a JEOL JEM-2200FS TEM operating at 200 kV equipped with a Gatan cryoholder.

Synthesis: All starting materials and solvents were purchased from Aldrich, Acros Organics or Beijing Chemicals and used as received unless otherwise stated. Milli-Q water (18.2M Ω cm) was used in all cases. The bolaamphiphile, N,N-icosanedioyl-di-L-histidine methyl esters (**BolaHis**) was synthesized by the amidation of L-histidine methyl ester with eicosanedioic acid. Yield=61%. ¹H NMR (400MHz, [D₆]-DMSO, 25°C, TMS): 1.23(s, 30H; CH₂), 1.41-1.44(m, 4H; CH₂), 2.04-2.08(t, ³J(H,H)=7.2 Hz, 4H), 2.79-2.92(m, 4H; CH₂), 3.58(s, 6H; CH₃), 4.43-4.48(q, ³J(H,H)=7 Hz, 2H; CH), 6.77(s, 2H; NH), 7.51(s, 2H; imi-C(4)H), 8.14 (s, 2H; imi-C(2)H), 11.80(s, 2H; imi-NH). MALDI-TOF-MS: m/z (%): 645.7 [M+H]⁺, 667.7 [M+Na]⁺, 683.7 [M+K]⁺. Elemental Analysis calcd(%) for C₃₄H₅₆N₆O₆: C 63.33, H 8.75, N 13.03; found: C 63.18, H 8.84, N 12.69.

Procedures: For the TEM and SEM measurements, a small amount of hydrogels were placed onto carbon coated copper grid (unstained) or single-crystal silicon plate (Pt coated) respectively after vacuum-dried for 12 hours. In the case of preparing samples for XRD measurements, gels were cast onto glass plates and dried in vacuum. Platelets made from the mixture of vacuum-dried xerogels with KBr powder and hydrogel sample nipped by CaF₂ platelets were used for FT-IR spectral measurements.

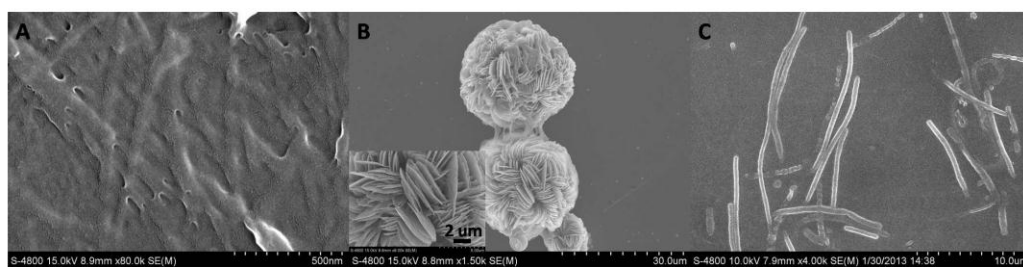


Figure S1: SEM images of self-assembled nanostructures (precipitates) formed by **BolaHis** with CoCl_2 (A), NiCl_2 (B), and ZnCl_2 (C).

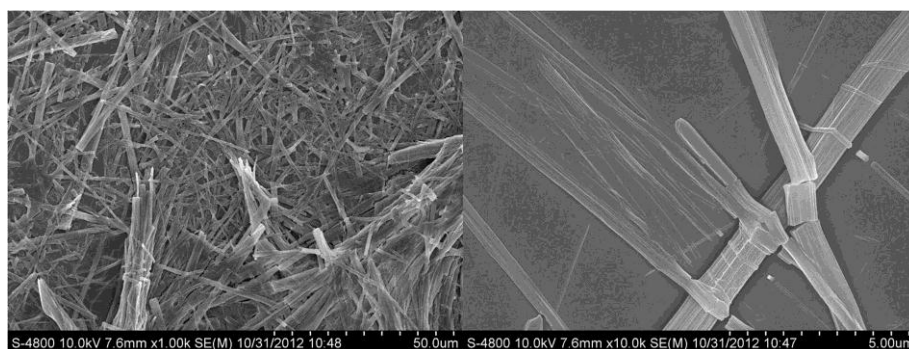


Figure S2: SEM images of hydrogel formed by **BolaHis** in 6M HCl solution.

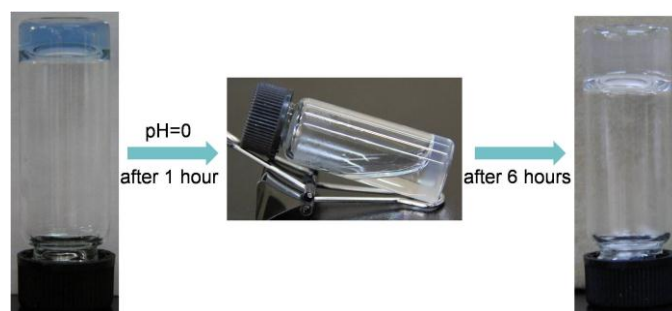


Figure S3: The photographs of transition process from **BolaHis**/ Cu^{2+} hydrogel to **BolaHis**/ H^+ hydrogel.