Supramolecular Copolymer from Two-component gels: Metal Ion-Mediated Cross-Linking, Enhanced Viscoelasticity and Supramolecular Yarn

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1: Experimental Section

Materials: 2, 2'-bipyridine-dicarboxylic acids were purchased from Sigma-Aldrich and used as received. Bolaamphiphilic L-histidine (**BolaHis**) was synthesized according to the method described in the literature. $CuCl_2$ and other metal salts were purchased from Acros Organics. All the other starting materials and solvents with analytical reagents grade were purchased from Beijing Chemicals. Milli-Q water (18.2 MΩ cm) was used in all cases.

Instruments: 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 2100F operating at accelerating voltages of 15 and 200 kV, respectively. JASCO UV-550 and JASCO J-810 CD spectrometers were used for the UV/Vis and CD spectral measurements, respectively. 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) measurements was performed on a Rigaku D/Max-2500 X-ray diffract meter (Japan) with Cu/Kα radiation (λ = 1.5406 Å), which was operated at 45 kV, 100 mA. Rheological studies were achieved on a Discovery DHR-1 Rheometer (TA Instruments).

Method: The supramolecular polymers were cast onto single-crystal silica plates (Pt coated) and carbon-coated Cu grids (unstained), and the water was evaporated at ambient conditions first, then vacuum-dried for 12 h for SEM and TEM measurements. The KBr pellets made from the vacuum-dried supramolecular polymers were used for FT-IR spectra measurements. The 2mm cuvette was used for UV-Vis spectra and CD spectra measurements. The quartz-plate-sustained supramolecular polymers films were used for X-ray diffraction (XRD) measurements. The rheological measurements were carried out on the Discovery DHR-1 Rheometer (TA Instruments) using parallel plate geometry in a Peltier plate. The diameter of plate is 40 mm, and the plate gap was set as 1000μm. The rheological properties of the samples were measured at 25.00 ℃. Two types of experiments were performed: (1) Dynamic frequency spectrum; In the frequency sweep experiment, the variation of storage modulus (G') and loss modulus (G'') was monitored as a function of applied angular frequency (from 1 to 100 rad s -1) under a constant strain 0.1%. (2) Steady shear rheology; the range of shear rate has been changed from 0.01 to 500 s-1. All samples were performed with BolaHis at a concentration of 0.1 wt%.

2: Supplementary Table and Figures

Table S1. Gelation ability of two-component supramolecular polymers in water

2,2'bipy/Bola	1:1	2:1	3:1	4:1
B3D	S	S	S	S
B4D	G	OG	OG	OG
B5D	TG	G	G	G
B6D	P	P	P	P

Concentration of **BolaHis**=0.1 wt%. P=precipitate; TG=transparent gel; OG=opaque gel; G=translucent gel; S=solution

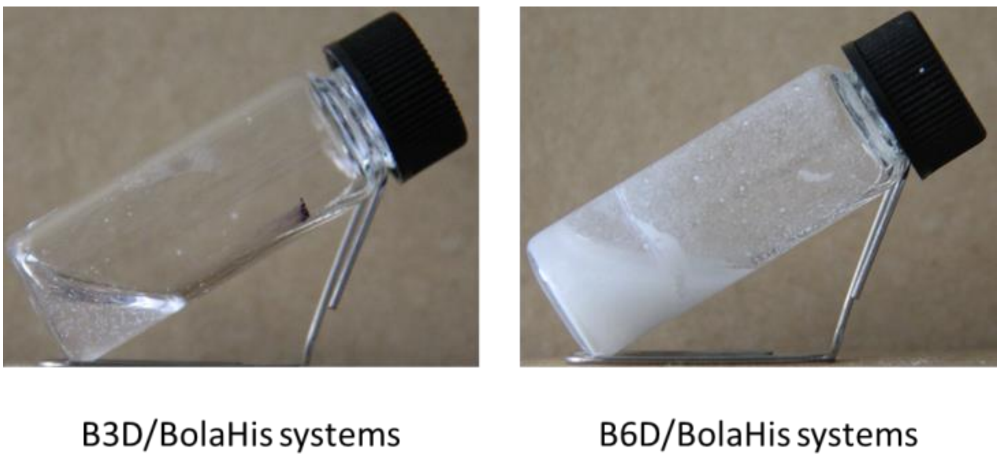

Figure S1: Photograph of **B3D**/**BolaHis** assemblies (left) and **B6D**/**BolaHis** assemblies (right).

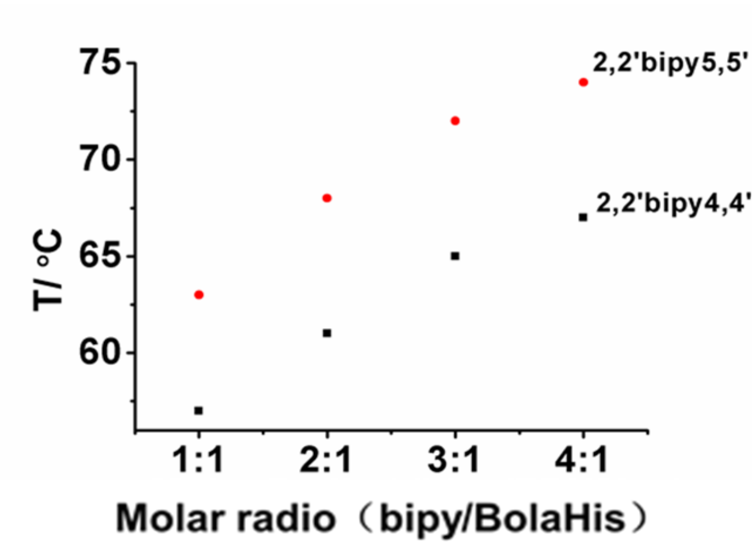

Figure S2: Sol–gel transition temperature (T_{gel}, ^{o}C) of hydrogels formed by **BolaHis** and 2, 2’-bipyridine-4, 4’-dicarboxylic acid (**B4D**) and 2, 2’-bipyridine-5, 5’-dicarboxylic acid (**B5D**)

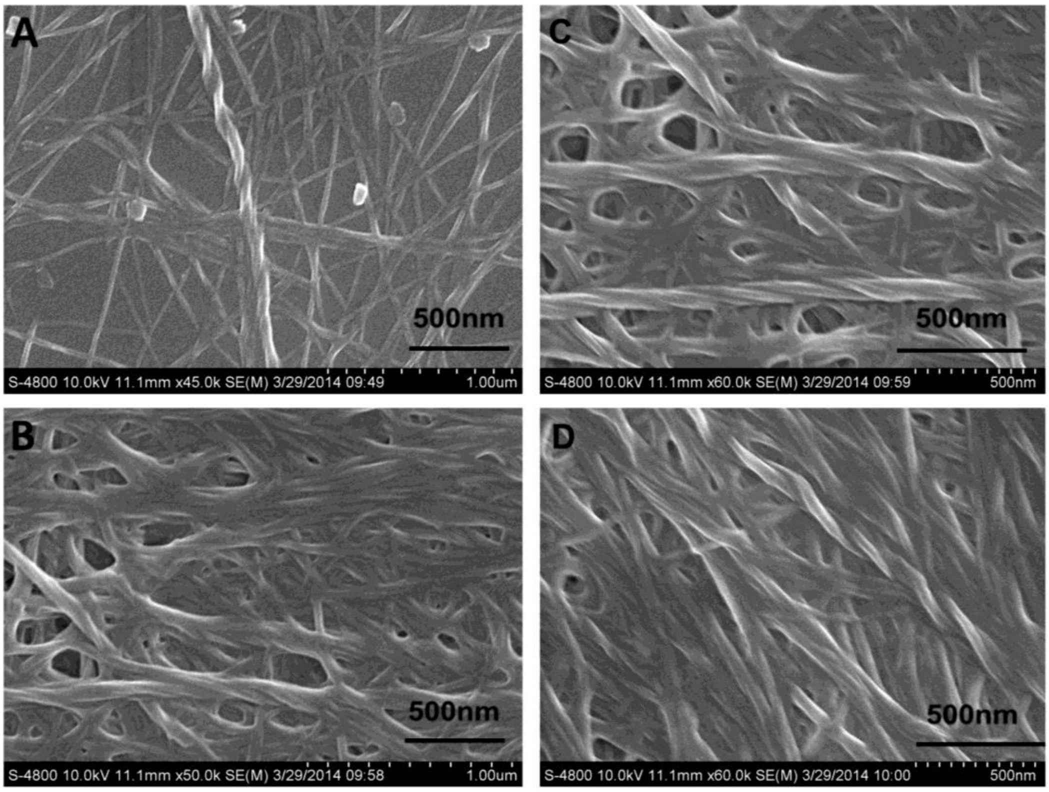

Figure S3: SEM images of two-component hydrogels formed by **B5D**/**BolaHis** (A, B); **B4D**/**BolaHis** (C, D).

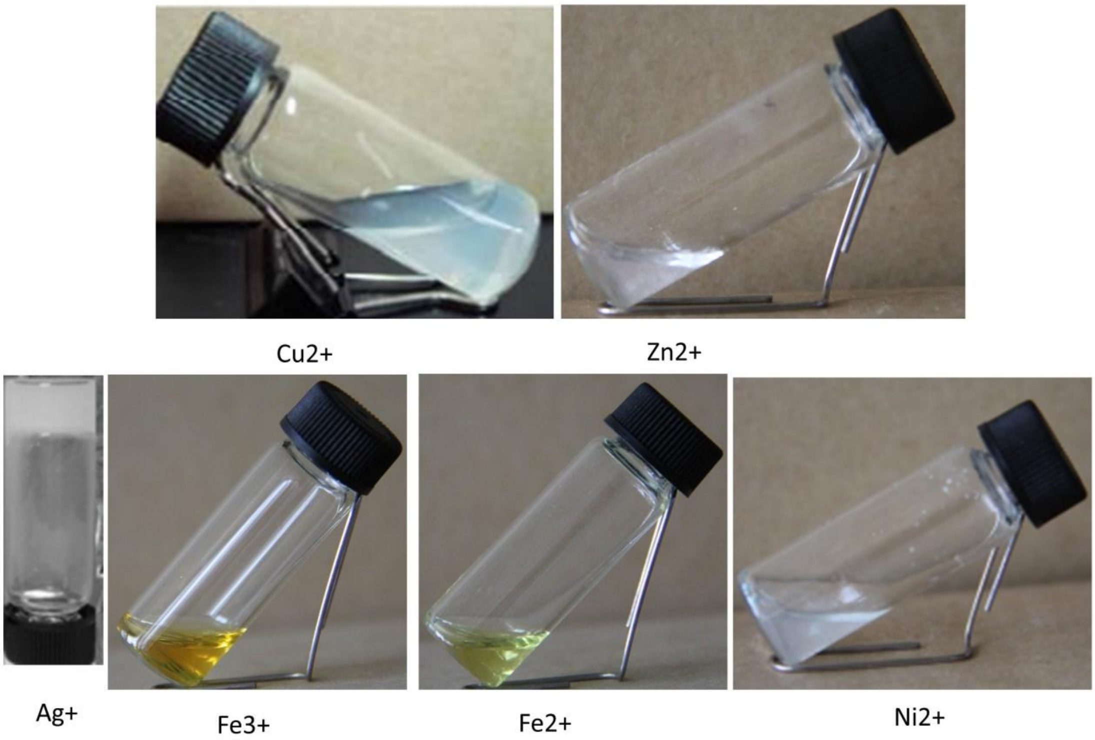

Figure S4: Photograph of **B5D**/**BolaHis** interacted with different metal ions.

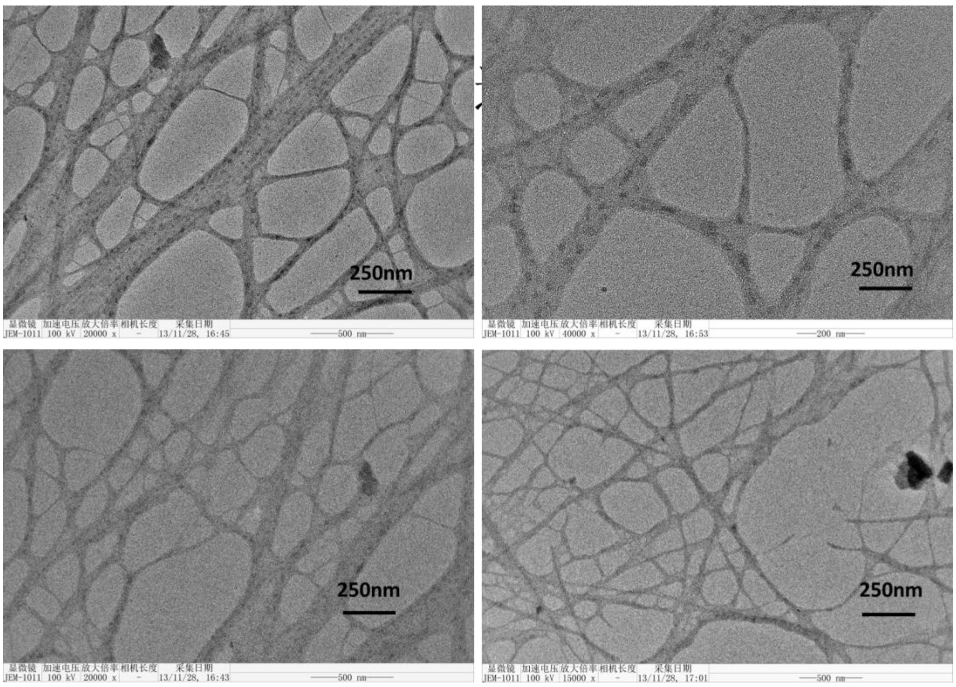

Figure S5: TEM images of $CuCl_2$/**B5D**/**BolaHis**=0.5/1/1 supramolecular polymer.

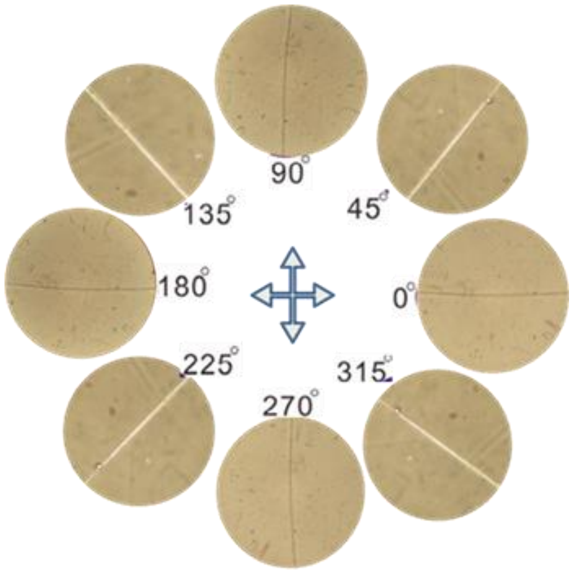

Figure S6: Cross-polarized microscope images of macroscopic supramolecular yarns.

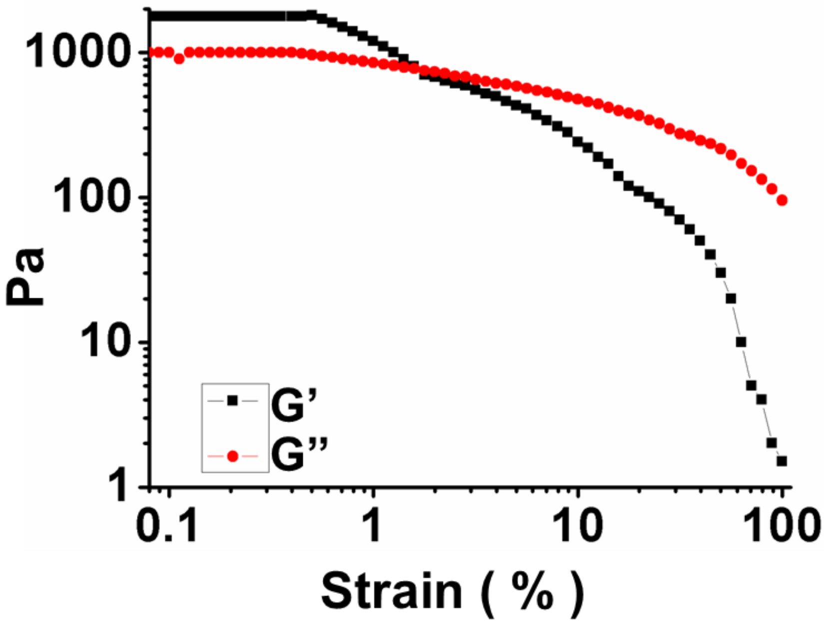

Figure S7. The Storage modulus G' and loss modulus G'' values of the **B5D/BolaHis** systems on rheological experiments of strain sweep

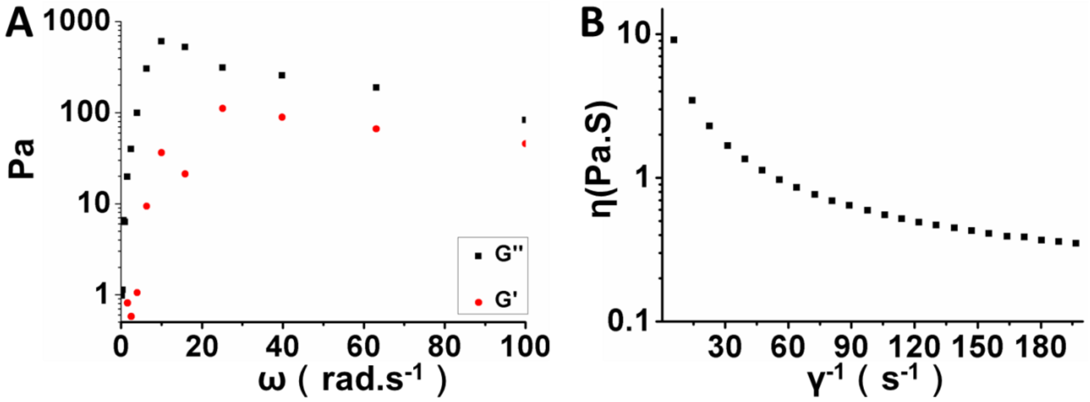

Figure S8: Rheological measurements on the aqueous solution of $ZnCl_2$/**B5D**/**BolaHis**=0.5/1/1. (A) Storage modulus G’ and loss modulus G’’ versus frequency ω (from 1 to 100 rad s^{-1}) (B) Shear rate dependence of viscosity.

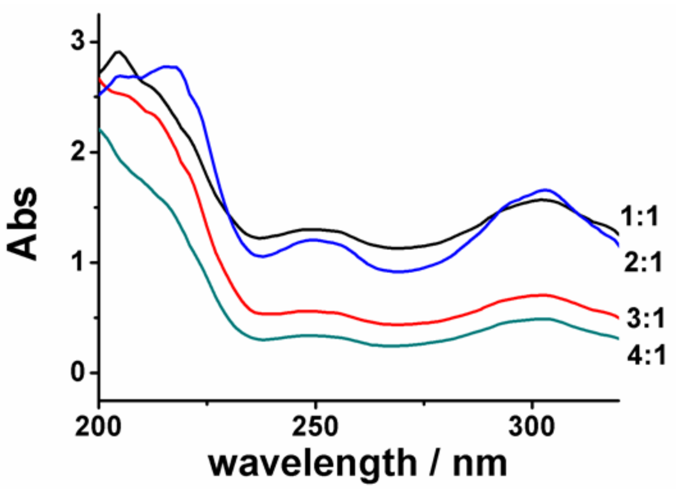

Figure S9: UV/Vis spectra of $CuCl_2$/**B5D**/**BolaHis** systems with different ratios.

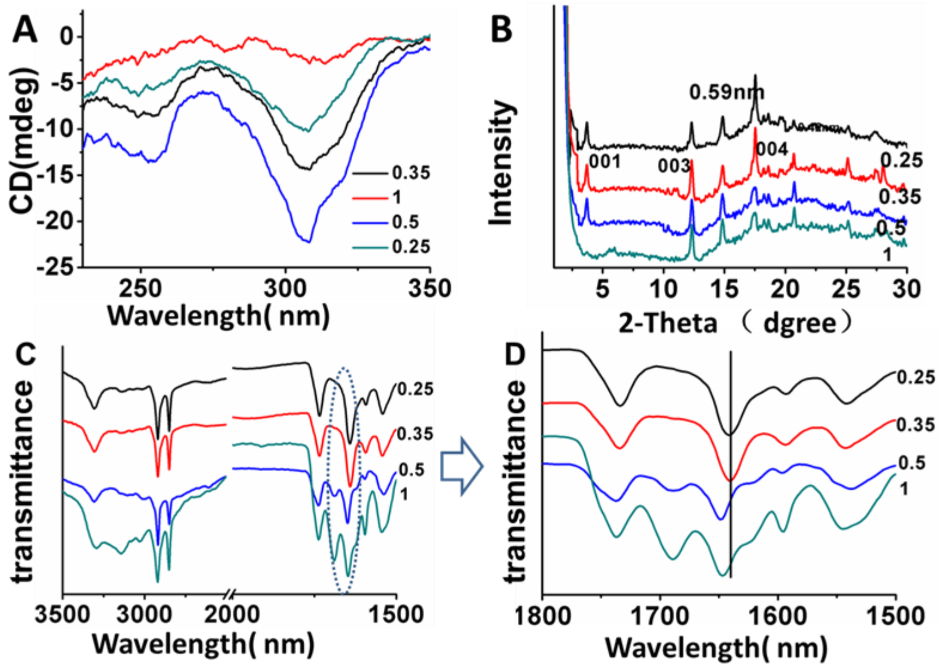

Figure S10: CD spectra (A), XRD pattern (B) and FT-IR spectra（C, D）of $CuCl_2$/**B5D**/**BolaHis** assemblies with different molar ratios. The molar ratios of **B5D**/**BolaHis** were kept as 1/1, and the quantity of $CuCl_2$ was changed from $CuCl_2$/**B5D**/**BolaHis**=0.25/1/1 to $CuCl_2$/**B5D**/**BolaHis**=1/1/1.

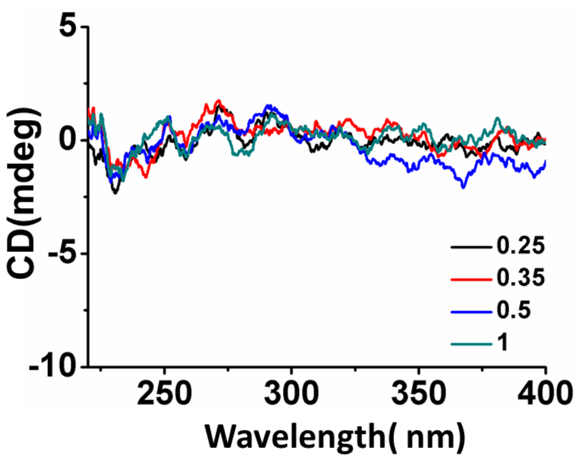

Figure S11: CD spectra of $ZnCl_2$/**B5D**/**BolaHis** assemblies. The molar ratios of **B5D**/**BolaHis** were kept as 1/1, and the quantity of $ZnCl_2$ was changed from $ZnCl_2$/**B5D**/**BolaHis**=0.25/1/1 to $ZnCl_2$/**B5D**/**BolaHis**=1/1/1.

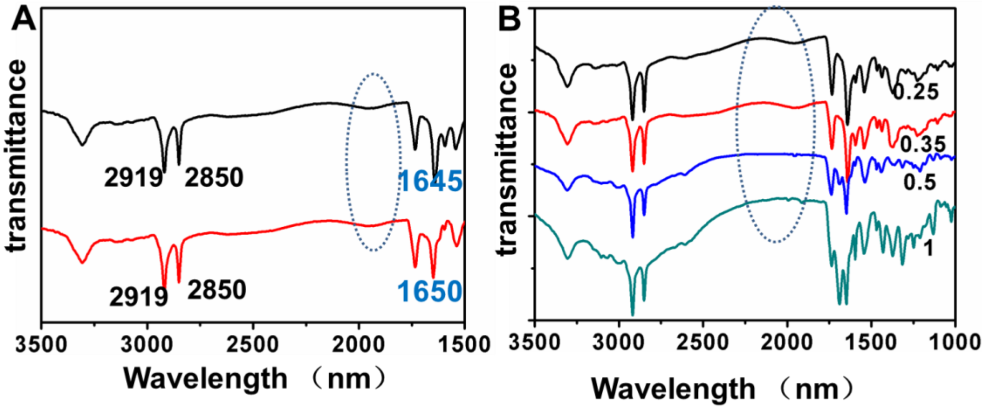

Figure S12: Enlarged FT-IR spectra for showing the broad band around 1940–1960 cm^{-1} from Figure 3B (A) and Figure S9C (B).

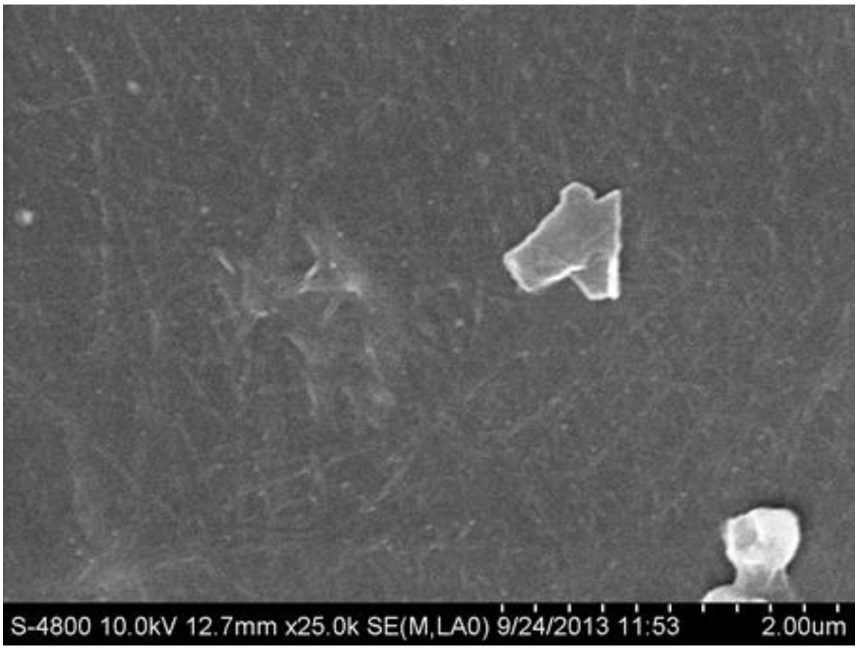

Figure S13: SEM images of $ZnCl_2$/**B5D**/**BolaHis**=0.5/1/1 supramolecular polymer. Fiber structures were basically formed. However, there are some larger structures, which could be the complex formed by the B5D and Zn2+.