Aggregation of highly charged nano-fibrils in different pH environments

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Introduction

- Nanofibrils with charged surface draw great attention not only because of novel and interesting conformational state and phase transitions but also on account of importance application in biological science such as mimic the natural fibration of bio-macromolecules and mediate important biological process like promote tissue regeneration 、 signaling. While advancing these importance application are limited because of the inherent difficulties in handling electrostatic interactions between charged nanoparticles so cannot freely control it aggregate and stabilization.

- Because of lack ideal samples most of the research about charged nonofibrils are based on computer simulation and theoretical calculation. It is urgent to use the experiment method quantified study how the factors (ion concentration、ion size、pH) tuned the interaction between the charged nano-structure and further more control their assembly properties.

- In this work we use a C3-symmetrical BTA molecular named $P_7(COONa)_3$(sodium carboxylate decorated three-armed aromatic oligoamide) which can spontaneous self-assembled into surface-charged helical nanofibrils, the nanofibrils then arrangement into 2D rectangle arrays in aqueous solution. Those well aligned nanofibrils provided as ideal research model system.
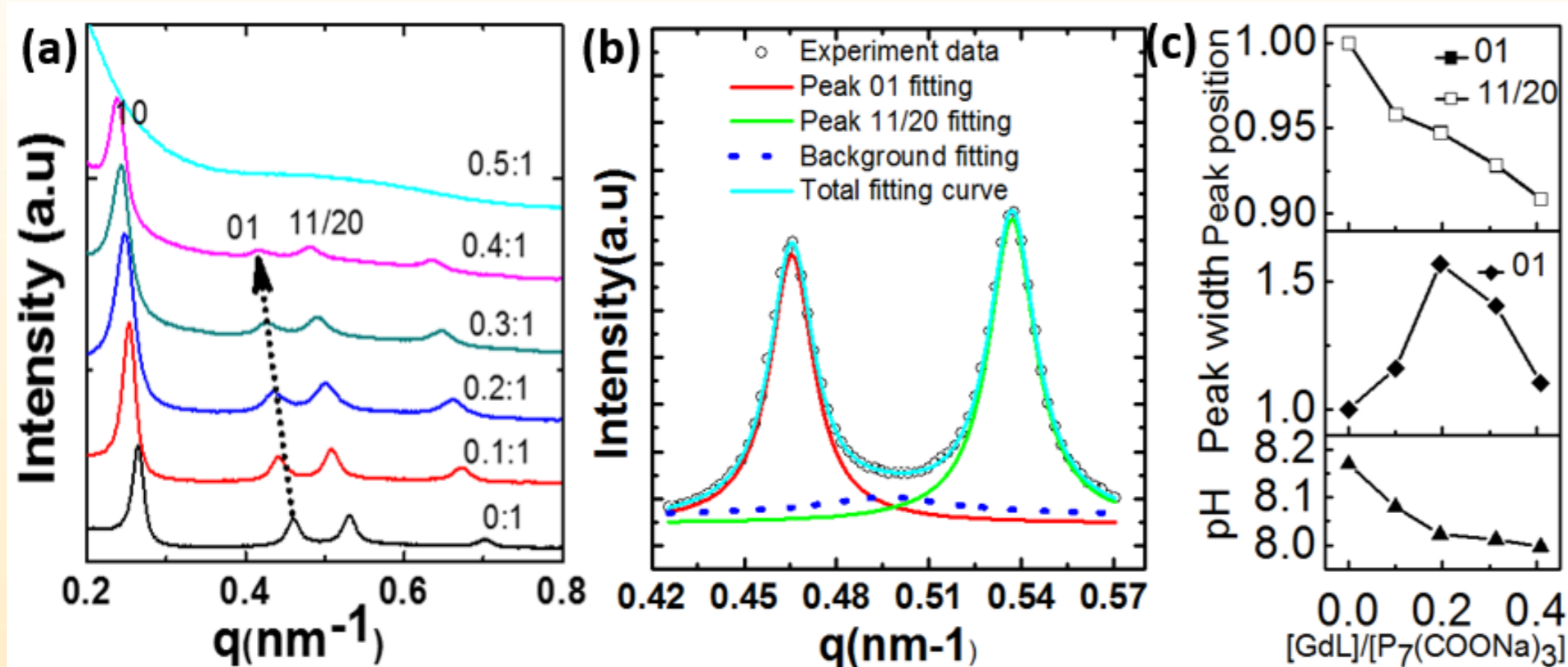
Experiments and data

Fig1 (a) 1D SAXS curves of different mole ratio of GdL to $P_7(COONa)_3$ in aqueous solution aged for three weeks;(b) Lorentz two peak fitting of 01 and 11/20 peaks after subtracting a broad peak(the blue dotted line) as background;(c) The parameters of scattering peaks and pH vs mole ratio of GdL to $P_7(COONa)_3$.All the numbers of peak position and peak width are scaled to pure 1.5wt% $P_7(COONa)_3$ in aqueous solution.
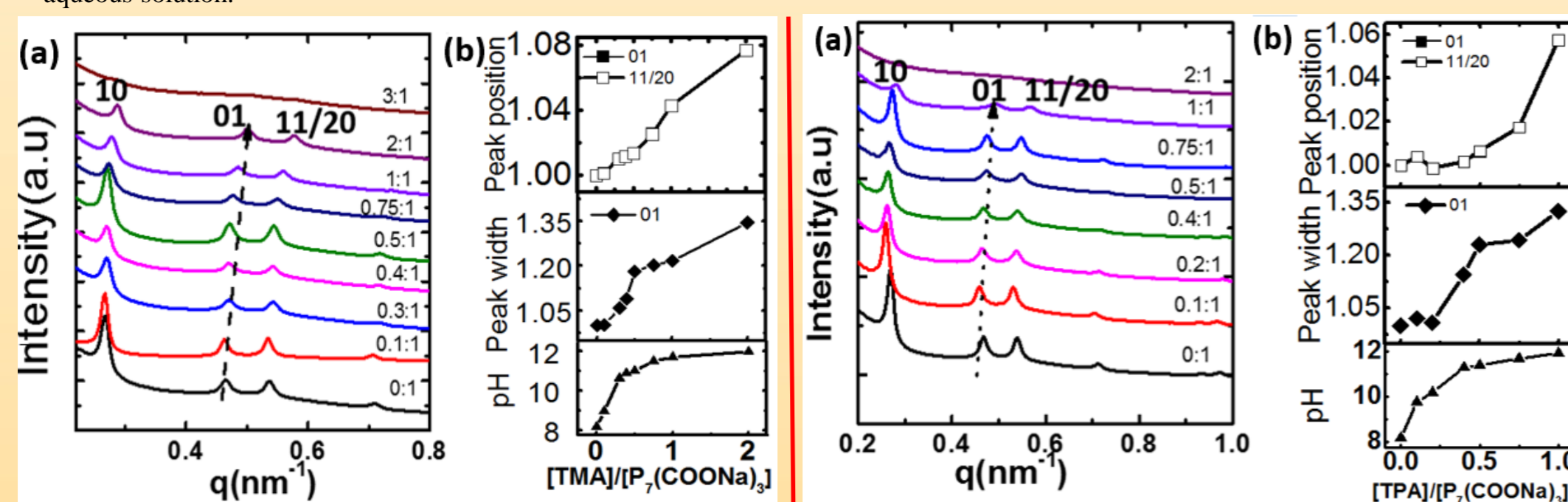

Fig.2 (a) 1D SAXS curves of different mole ratio of TMAOH (left) and TPAOH(right) to P7(COONa)3 in aqueous solution aged for three weeks. The dashed line highlight the change of peak position; (b) The parameters of scattering peaks and pH vs mole ratio of TMAOH or TPAOH to P7(COONa)3.All the numbers of peak position and peak width are scaled to pure 1.5wt% P7(COONa)3 in aqueous solution.
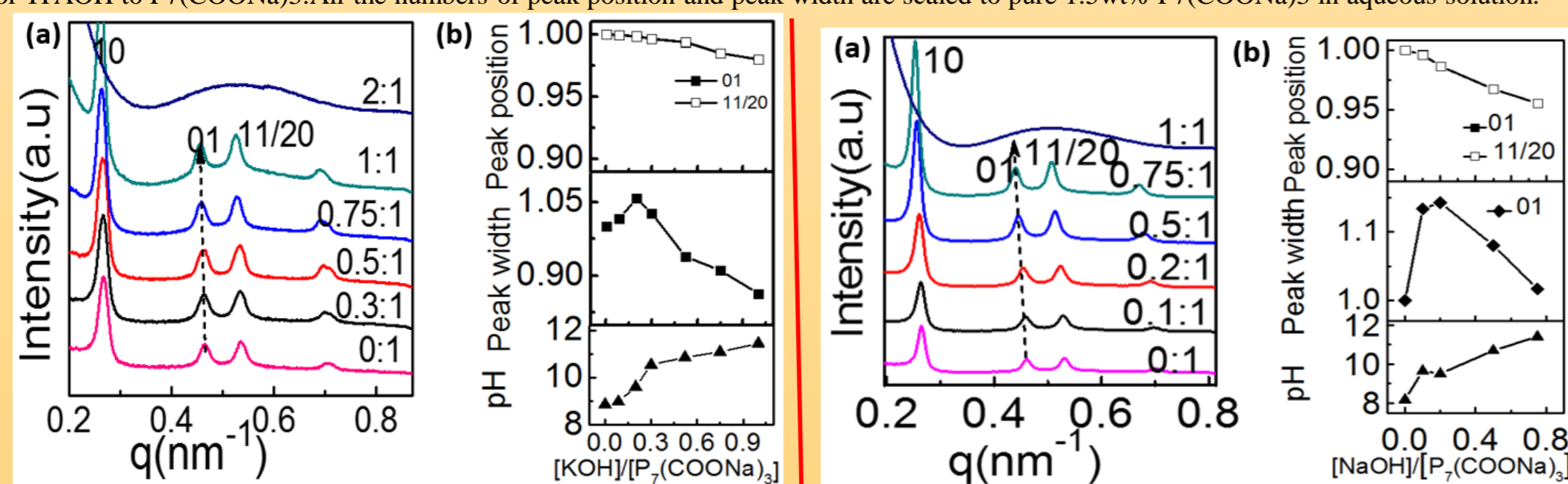

Fig.3 (a) 1D SAXS curves of different mole ratio of KOH(left) and NaOH(right) to $P_7(COONa)_3$ in aqueous solution aged for three weeks. The dashed line highlight the change of peak position; (b) The parameters of scattering peaks and pH vs mole ratio of KOH or NaOH to $P_7(COONa)_3$.All the numbers of peak position and peak width are scaled to pure 1.5wt% $P_7(COONa)_3$ in aqueous solution.

Methods

- Synchrotron radiation small angle X-ray scattering (SAXS) were performed at beamline 16B1 in Shanghai Synchrotron Radiation Facility with a radiation X-ray wavelength of 0.124nm ,and a Mar165 CCD detector was used to obtain the 2D SAXS patterns. Fit2D software package was used to transform the 2D SAXS patterns to 1D scattering vector vs scattering intensity SAXS curve where the scattering vector $q = 4\pi\sin\theta/\lambda$ (2θ is the scattering angle and λ is the X-ray wavelength).

- pH values were measured by Mettler Toledo FE20 armed with a Inlab Micro Pro electrode, pH range of the pH meter is 0.00 to 14.00、pH-relative accuracy is ∓0.01.

Discussion and Conclusion
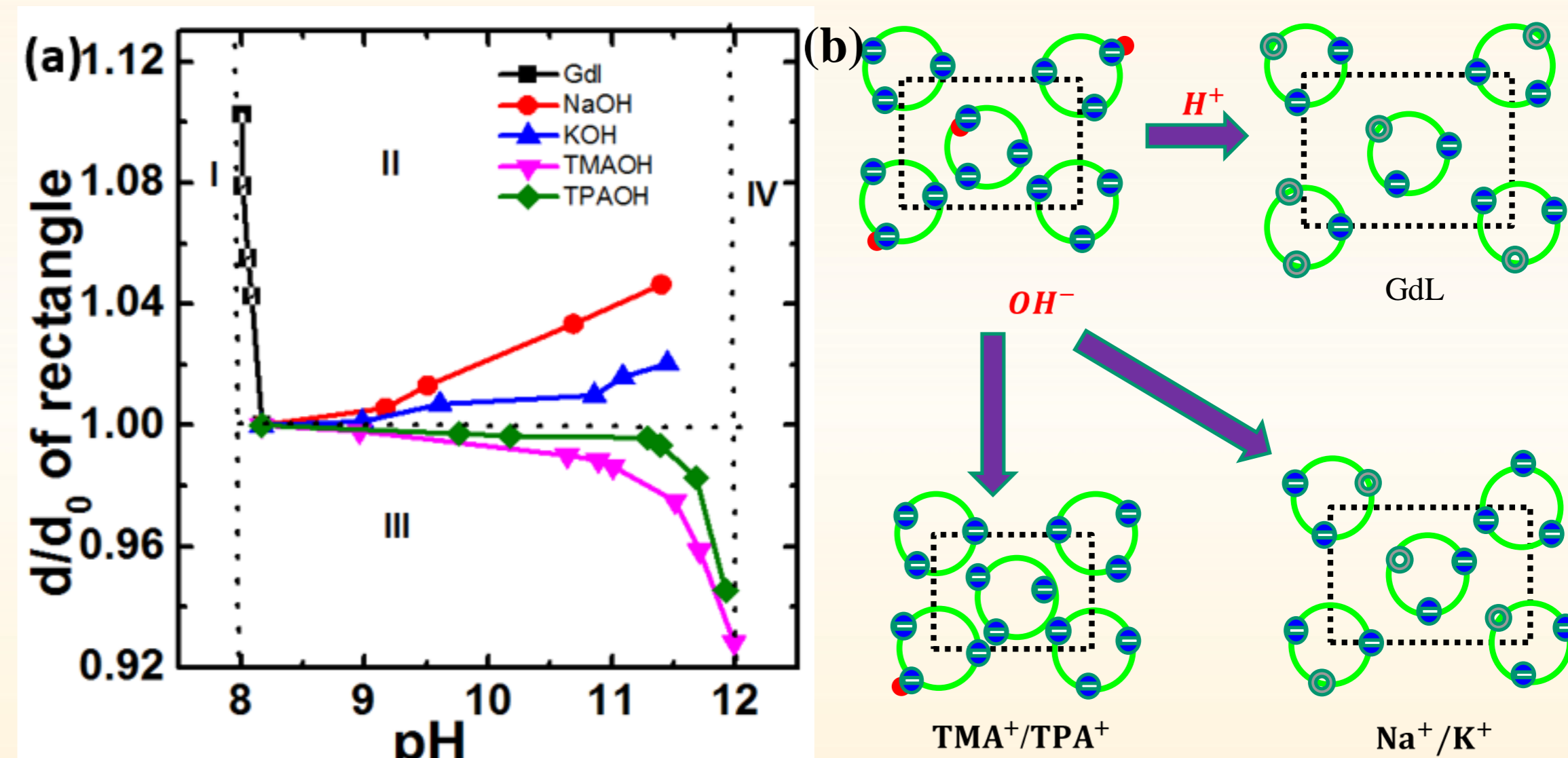

Fig.4 The distance between nano-fibrils of 1.5wt% $P_7(COONa)_3$ in aqueous solution of GdL、NaOH and KOH respectively vs the pH value of each system. Note that all the distance are scaled to the distance of pure 1.5wt% $P_7(COONa)_3$ in aqueous solution. In the region of I(pH<8.0) and IV the arrangement of rectangle array disappear, in the region of II the rectangle lattice expansion , in the region of III the rectangle lattice compression

Fig.5 Schematic of modification on surface charges along the supra-molecular nanofibrils and consequent evolution of the aggregation of nanofibrils in different pH. The dark-green rim describing the cylindrical wall composed by $P_7(COONa)_3$ molecules. The negative charged -COO^- groups on the nanofibrils surfaces are denoted by blue circles with a minus sign and the proton by red circles and the neutralized carboxyl by yellow ring. The position and size of the ions are only schematic and not to scale.

- When in acid environment the proton released by the added acid can protonated the carboxyl and decrement the surface charge density which promote the decrement of inter-fibrils attraction thus lead to the expansion of the rectangle lattice.

- When in alkali environment the hydroxyl will suppress the hydrolysis of carboxyl promote the increase of the surface charge thus lead to the compression of the rectangle lattice trend to be more aggregation .

- In alkali environment the cations have more complicated effect depend on the match degree of hydration energy between the cations and anion .

- The match degree of hydration energy between the cations and anion follow the rule: $Na^+ > K^+ \gg TMA^+/TPA^+$

Publication or other achievement

Shenghui Wei, et al, Aggregation of highly charged nano-fibrils in different pH environments . (in preparation)