Supporting information

Mechanistic process understanding of the self-assembling behaviour of asymmetric bolaamphiphilic short-peptides and their templating for silica and titania nanomaterials

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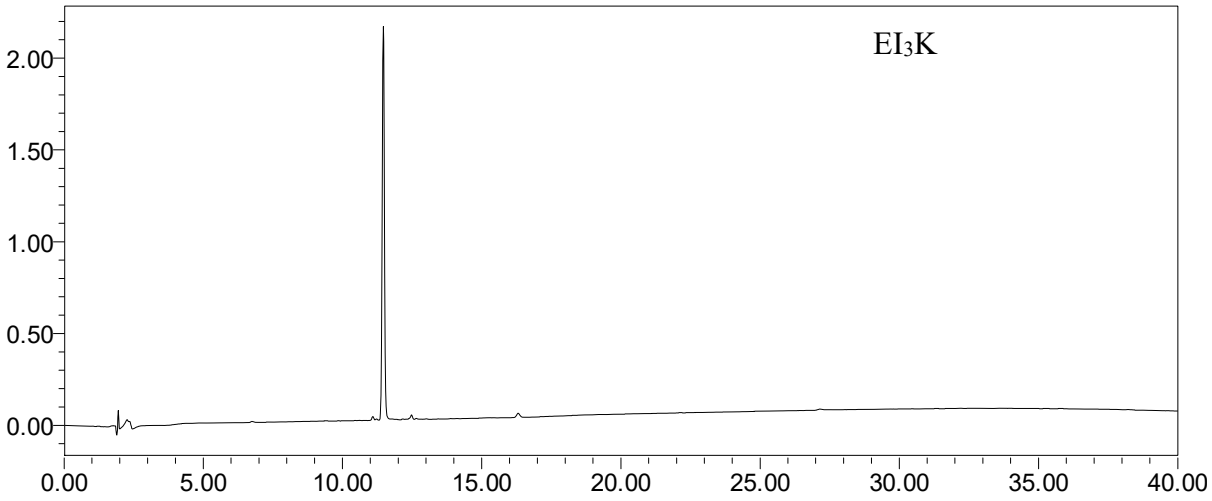
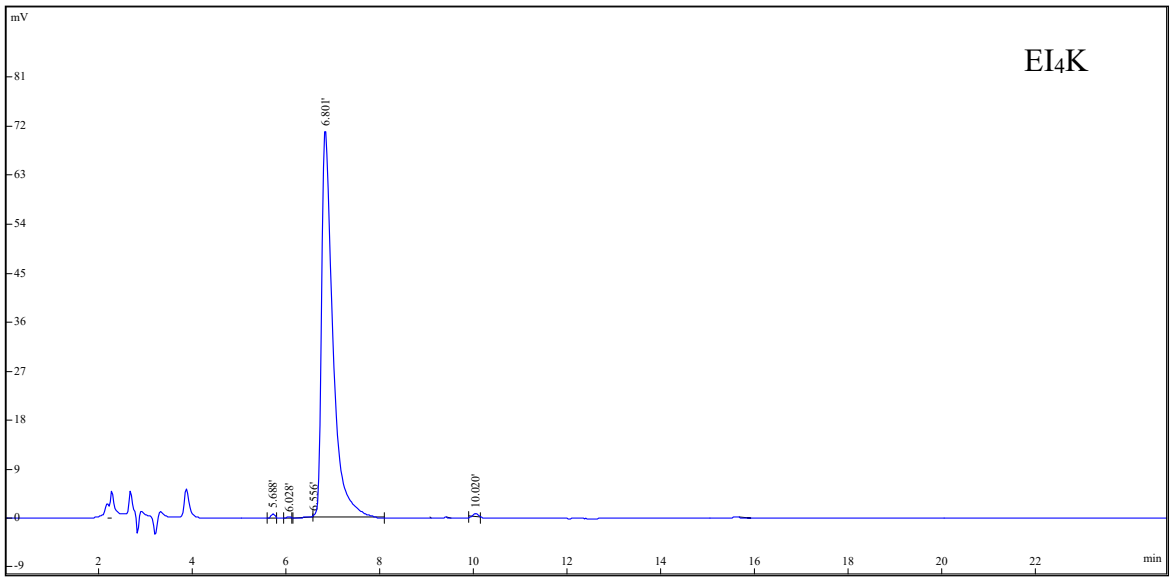
Supporting figures





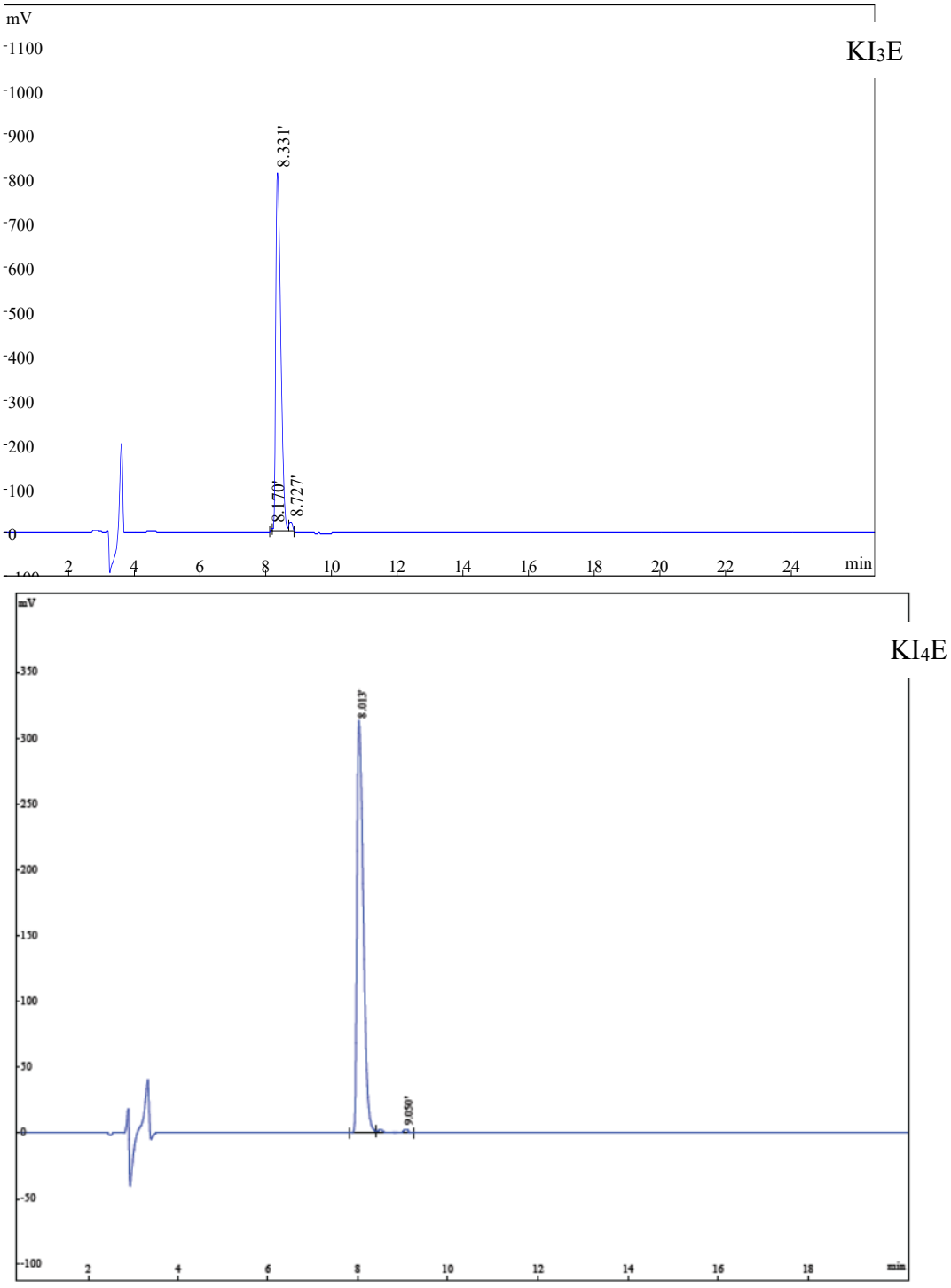
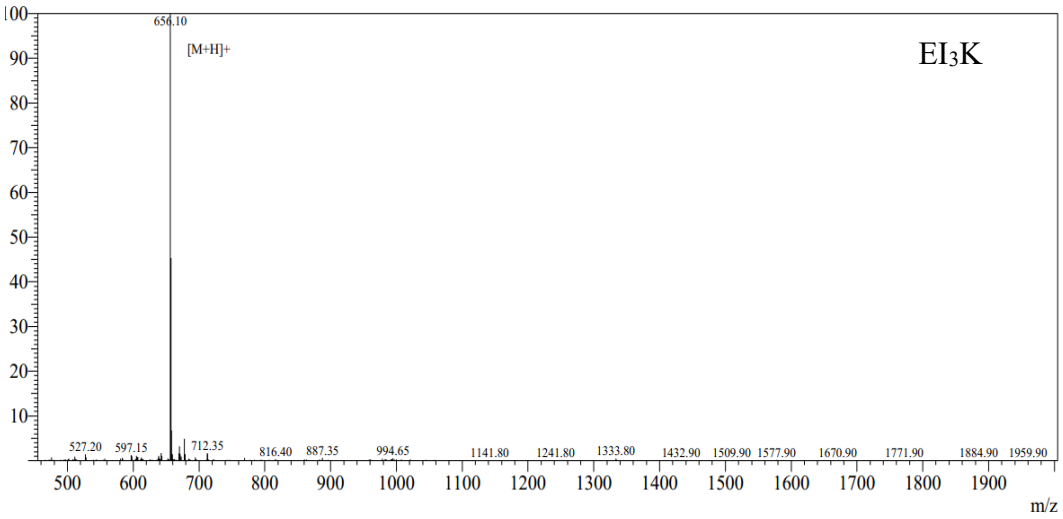


Figure S1 HPLC profiles of EI_3K, EI_4K, KI_3E and KI_4E. The conditions for the HPLC analysis are shown as follows: Eluent A, 0.1% TFA in acetonitrile; eluent B, 0.1% TFA in water. UV, 214 nm; flow rate, 1 mL min^{-1}. Inj. Vol., 10 μL. Column, Kromasil 100-5C18, 4.6 mm * 250 mm. The measurements were performed on a Waters 2695 Alliance HPLC system at 30 ºC.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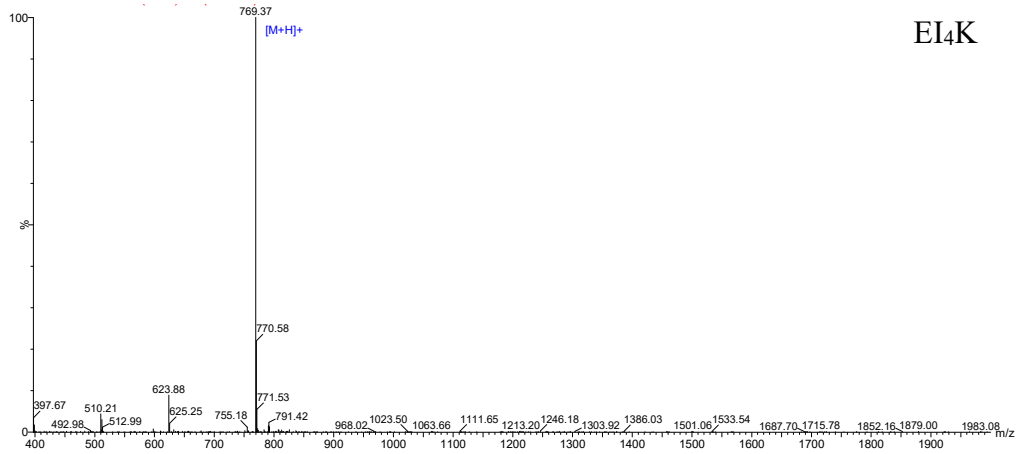
[M+H]+
EI3K
m/z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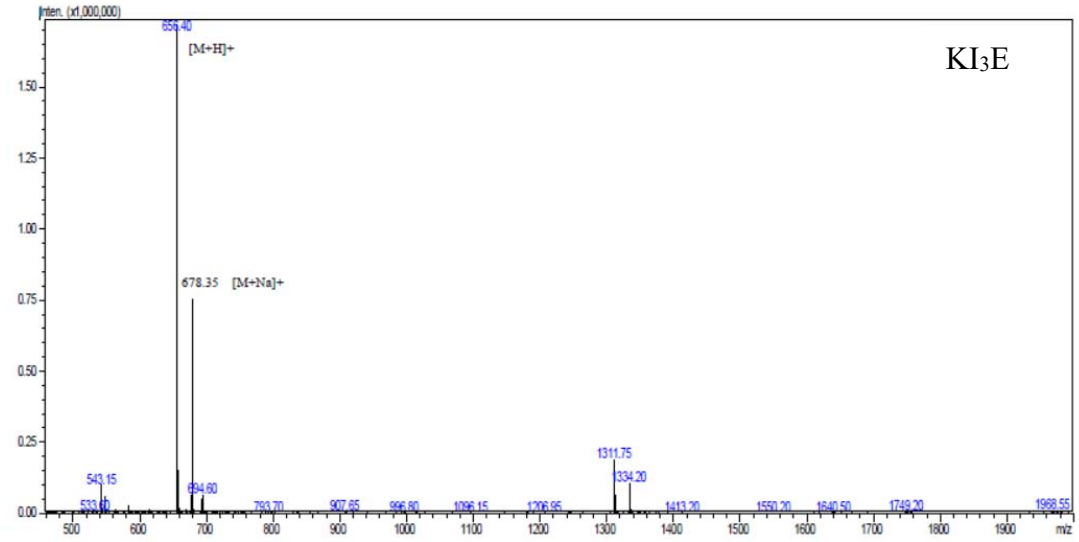
EI4K
%
m/z


Inten. (x1,000,000)
656.40
[M+H]+
KI3E
678.35 [M+Na]+
m/z

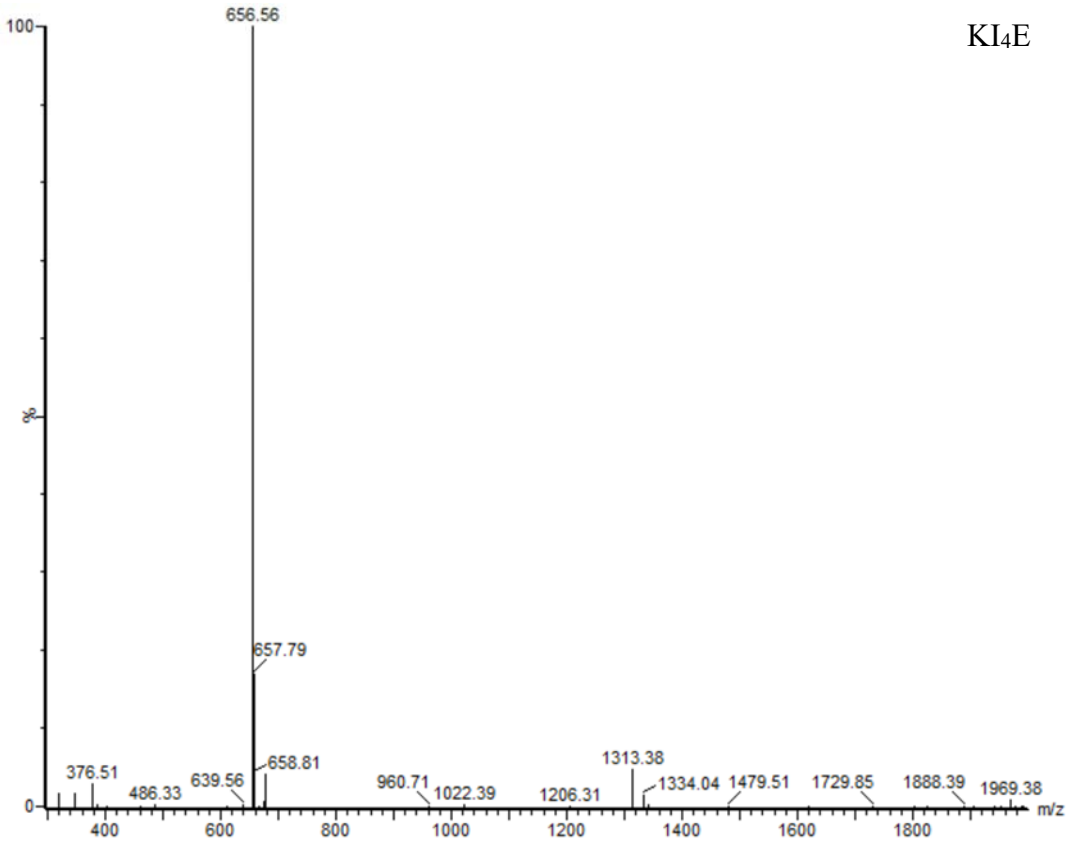


Figure S2 ESI MS spectra of EI_3K, EI_4K, KI_3E and KI_4E. The measurements were conducted on a LCMS-2010 instrument. ESI Capillary(KV): ± (2500~3000). Desolvation(L/hr): 800. Desolvation Temp: 450℃. Cone(V): 30~50. Run Time: 1 min.

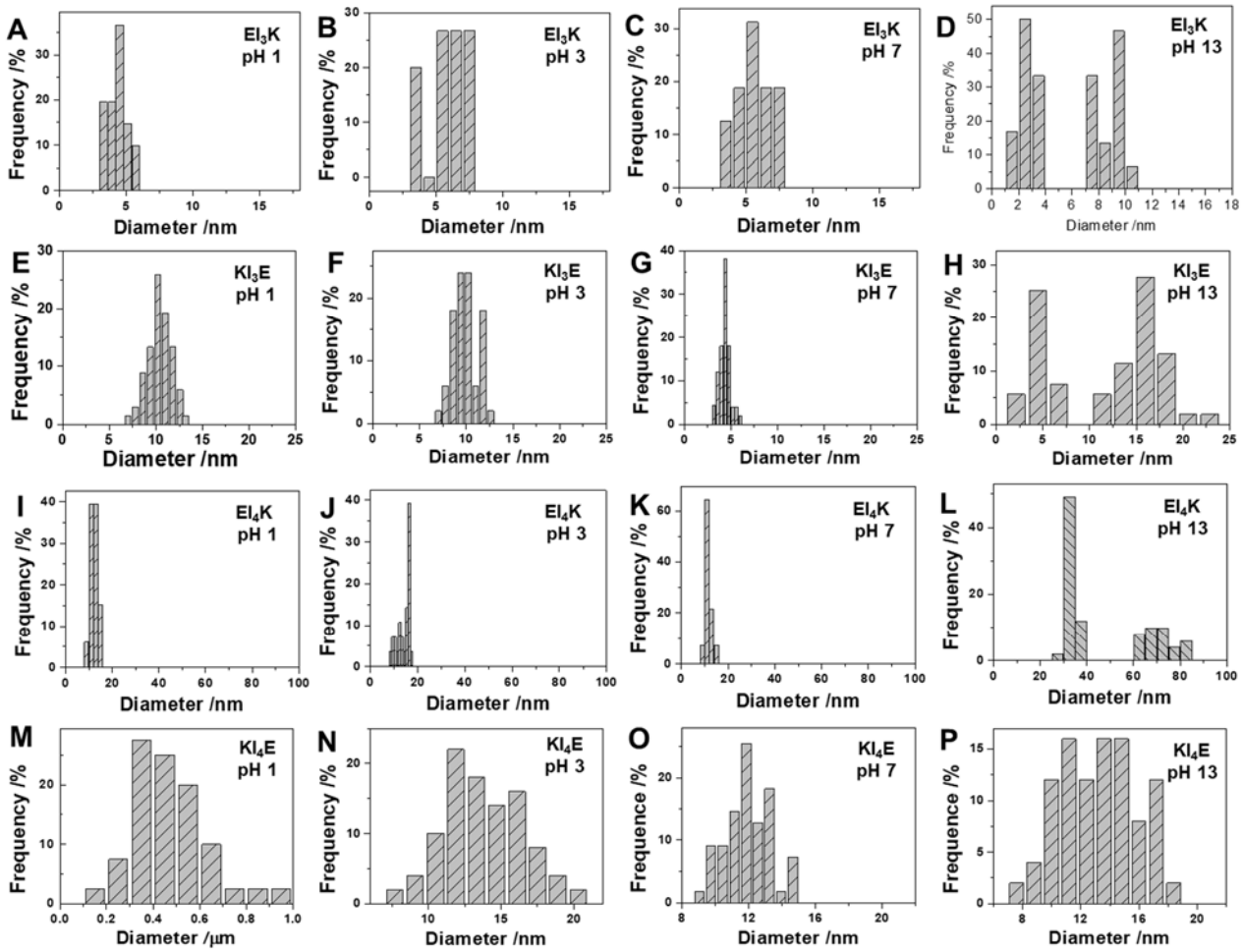


Figure S3 Diameter statistics of the self-assembled peptides structures formed at different pH. It needs noting that the diameters are determined from their TEM images (Figure 1).

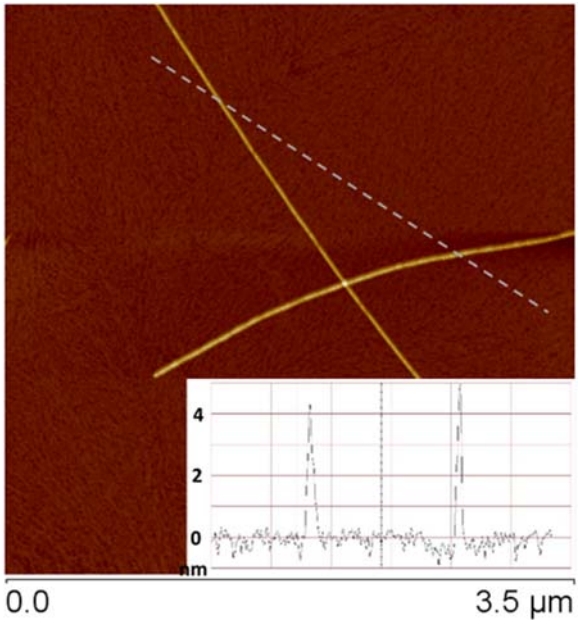


Figure S4 AFM image of EI_3K self-assembled structures formed at pH 3 for two weeks. Inset in panel A is the cross-sectional profile of EI_3K self-assembled structures.

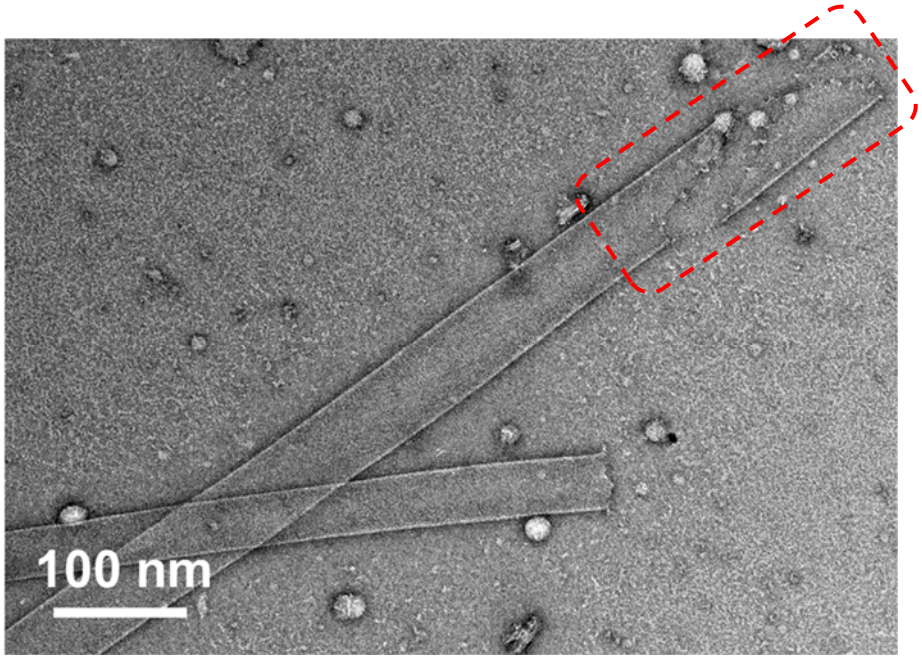


Figure S5 TEM image of EI_4K formed at pH 13. The unclosed terminus of the nanostructure (inside the red box) indicated that it was nanotubes enclosed by lamellar structures.

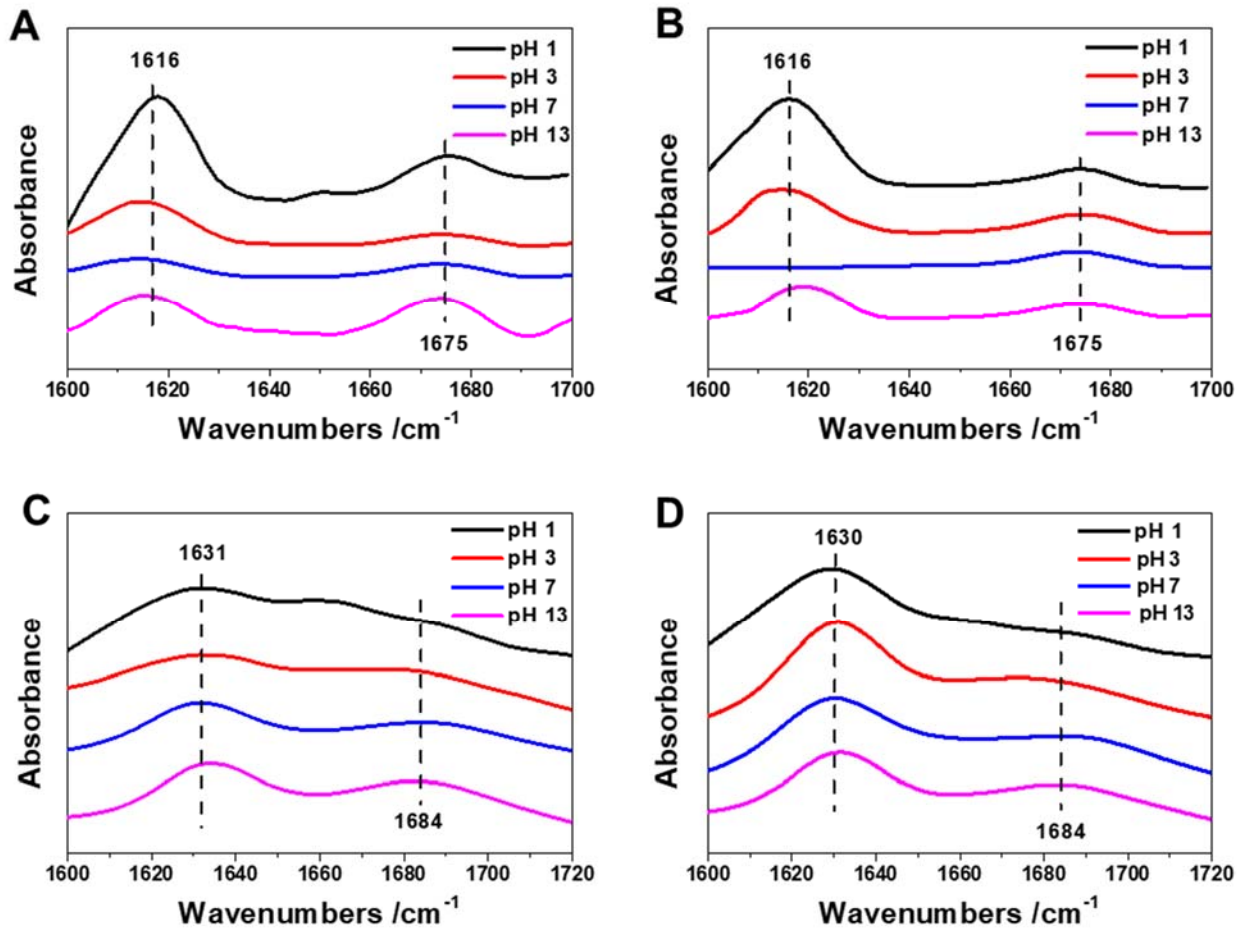


Figure S6 FTIR spectra of EI_3K (A), EI_4K (B), KI_3E (C) and KI_4E (D) at different pH.

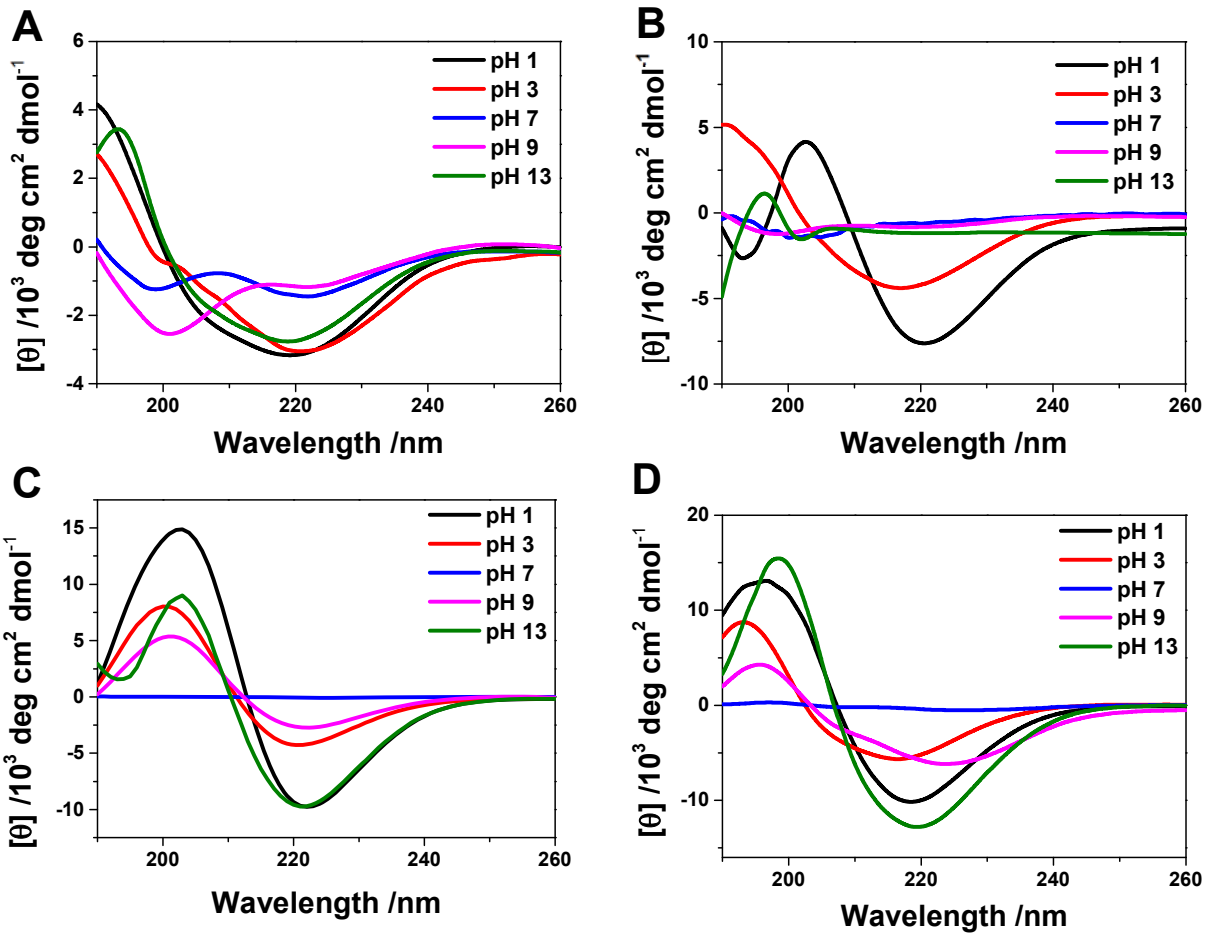


Figure S7 CD spectra of EI_3K (A), KI_3E (B), EI_4K (C) and KI_4E (D) at different pH

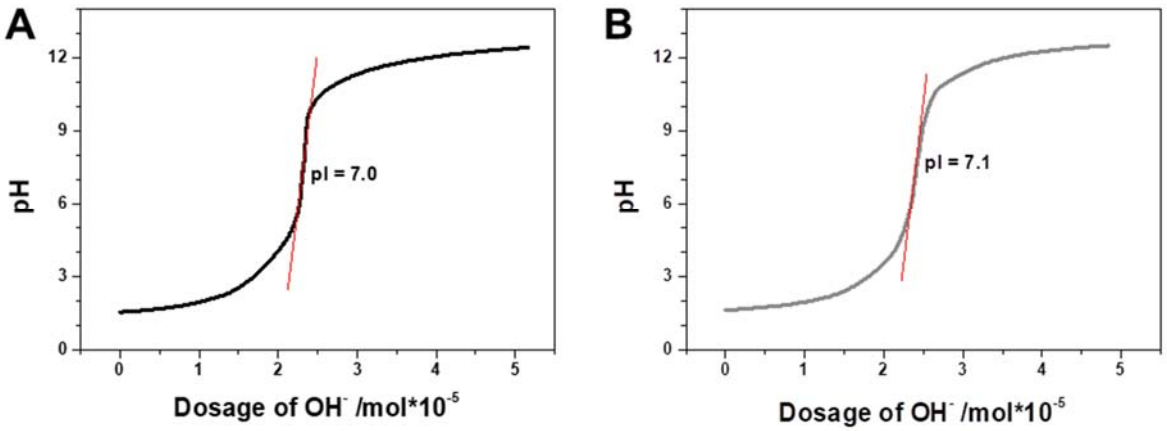


Figure S8 Determination of isoelectric point (pI) of EI_3K (A) and EI_4K (B) via acid-basic titration method. The detailed measurement was list as follows: the dilute NaOH solution of known concentration was gradually added to the acidic peptide solution (pH < 2) until the solution pH greater than 12, and the pH was plotted against the accumulated quantity of NaOH solution. Then the isoelectric point was determined according to the slope of the curves.

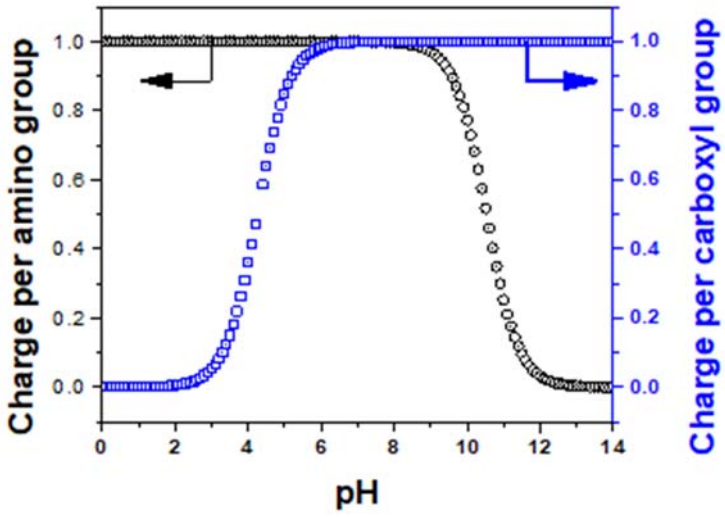


Figure S9 Influence of pH on the charge degree of aminol group in Lys and carboxyl group in Glu.

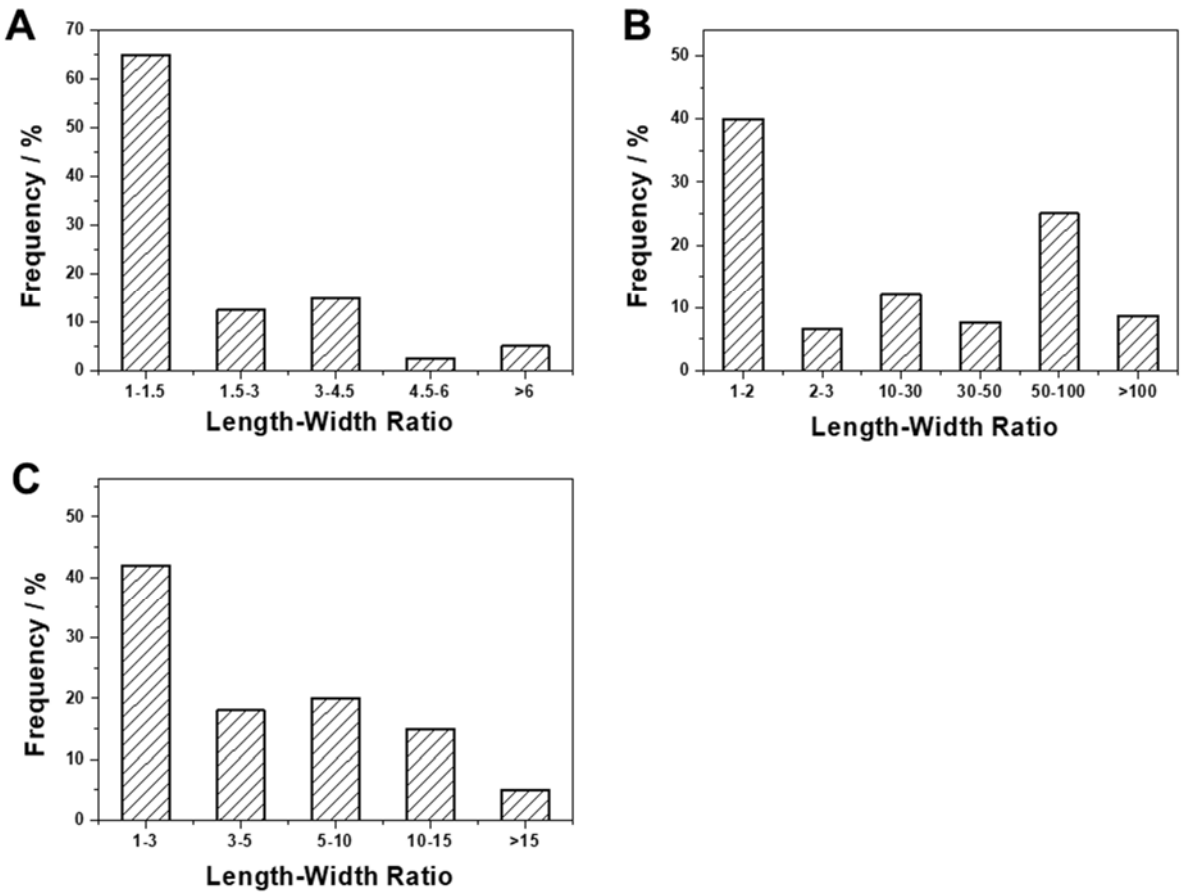


Figure S10 Statistics of length-width ratio of the self-assembled nanostructures aging for 2 days (A), 5 days (B) and 10 days (C). It needs noting that the statistics of random aggregates may be greater than their actual ratio because it is smaller than other structures and the statistics are based on the number of aggregates rather than their mole number. This resulted in differences between the statistics and the visual sense although both of them originated from same AFM images (Figure 2).

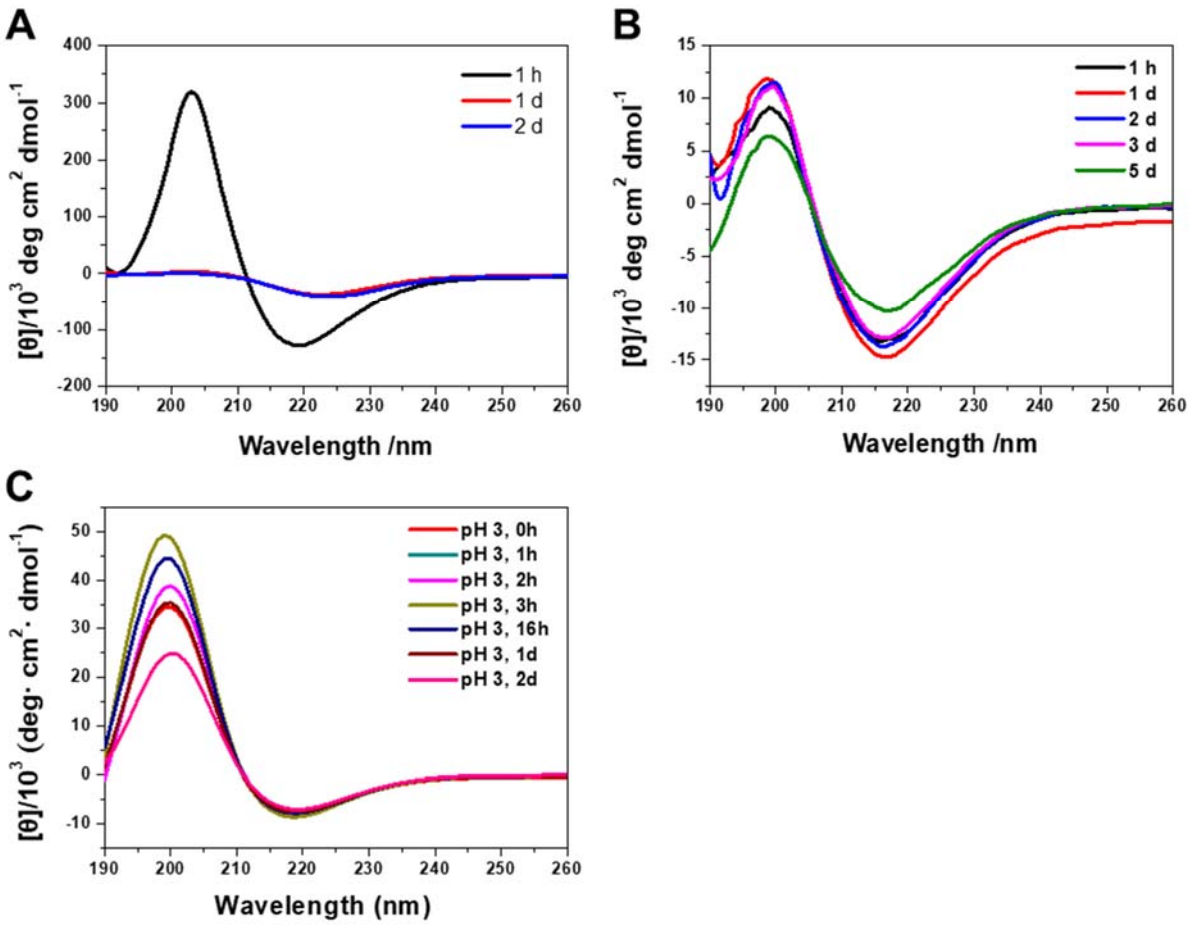


Figure S11 CD spectra of the preassembled EI_4K solution was adjusted from pH 13 to pH 3 (A), from pH 3 to pH 13 (B) and aging for different time. CD spectra of the preassembled KI_4E solution was adjusted from pH 1 to pH 3 and aging for different time (C).

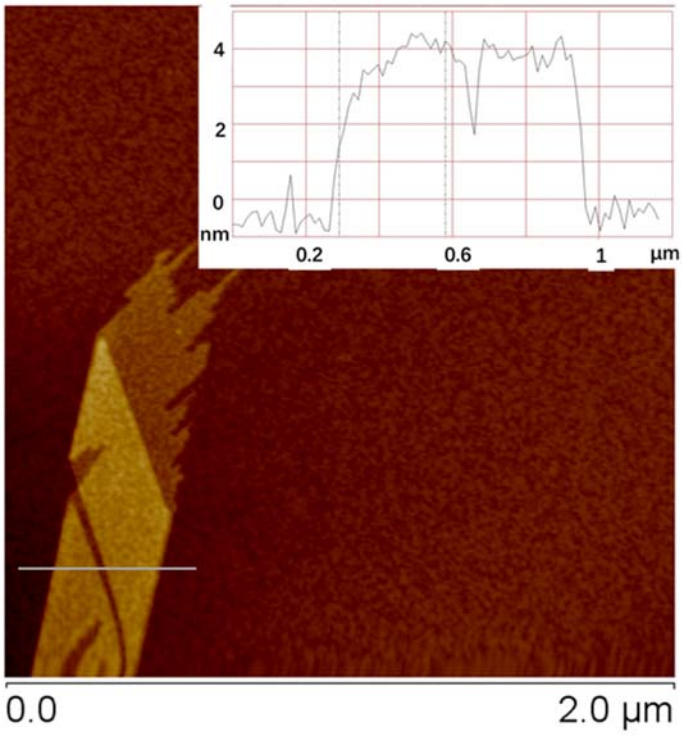


Figure S12 AFM image of the KI_4E unclosed nanotubes and the cross-section profiles (inset) showed that the KI_4E tubular structures were formed via helical ribbons intermediates containing the peptide monolayer.

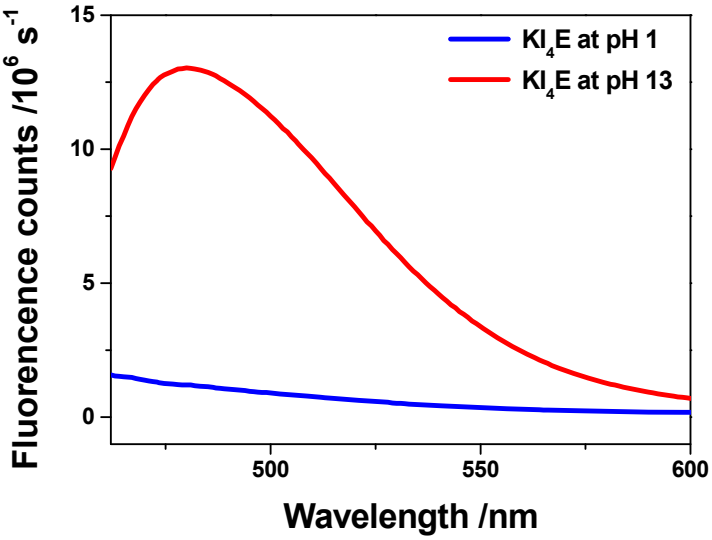


Figure S13 Fluorescence emission spectra (λ_{exc} = 440 nm) of ThT in the presence of KI_4E. it needs noting that no fluorescence contribution from ThT alone or KI_4E alone in the indicated wavelength range.

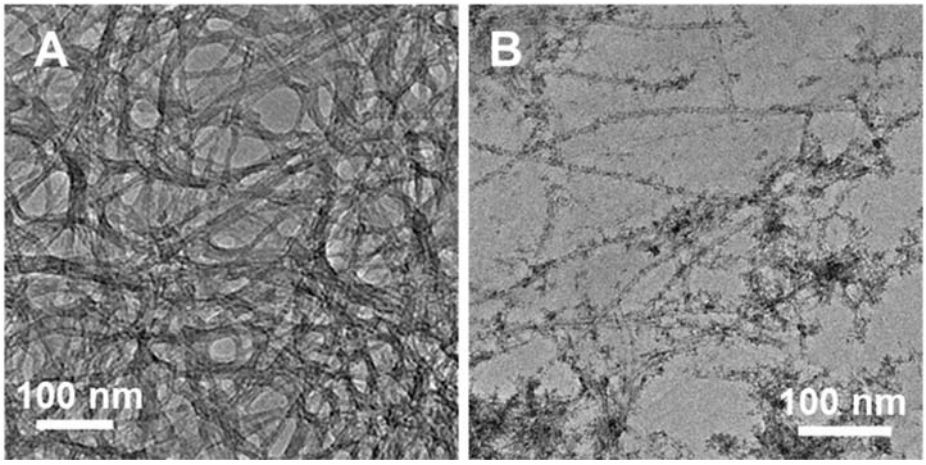


Figure S14 TEM images of silica nanostructures mediated by EI_3K self-assemblies at pH 8 (A) and titatia mediated by KI_3E self-assemblies at pH 10.

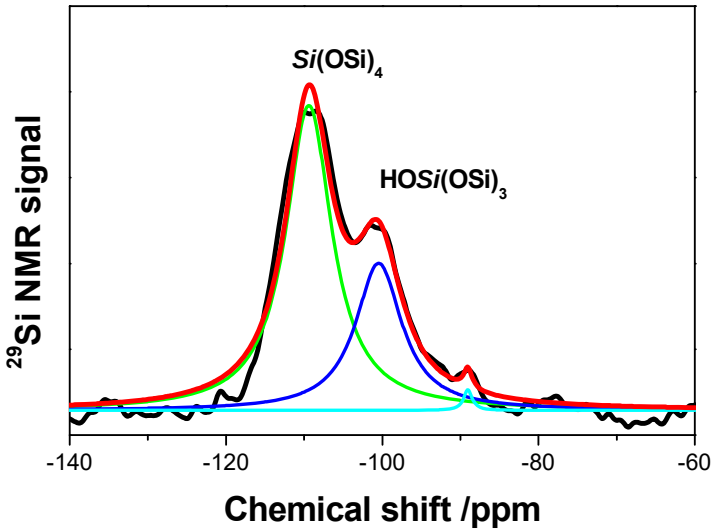


Figure S15 Solid-dtate ^{29}Si MAS NMR spectra of silica hybrids using EI_3K as template at pH 7. Peaks centered at -109.4 and 100.4 should be assigned to ***Si***$(OSi)_4$ and HO***Si***$(OSi)_3$, respectively.

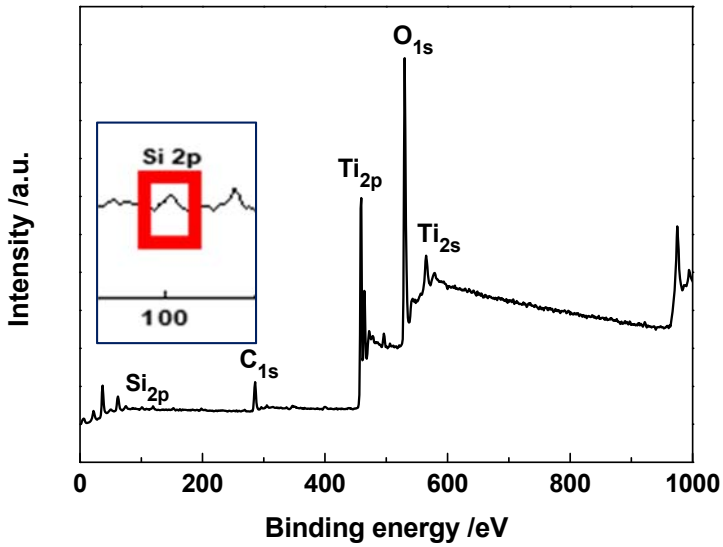


Figure S16 The survey XPS spectrum of the APTES directed synthesis of titania templated by KI_3E self-assembled structures, suggesting the coexistence of Si, Ti, C and O elements in the synthesized nanostructures.