

## Electronic Supplementary Information

# Enzyme-substrate interactions promote the self-assembly of amino acid derivatives into supramolecular hydrogels

Yanyan Xie<sup>b</sup>, Renliang Huang<sup>a,\*</sup>, Wei Qi<sup>b,c,d,\*</sup>, Yuefei Wang<sup>b</sup>, Rongxin Su<sup>b,c,d</sup>, Zhimin He<sup>b</sup>

<sup>a</sup> School of Environmental Science and Engineering, Tianjin University, Tianjin, 300072, PR China

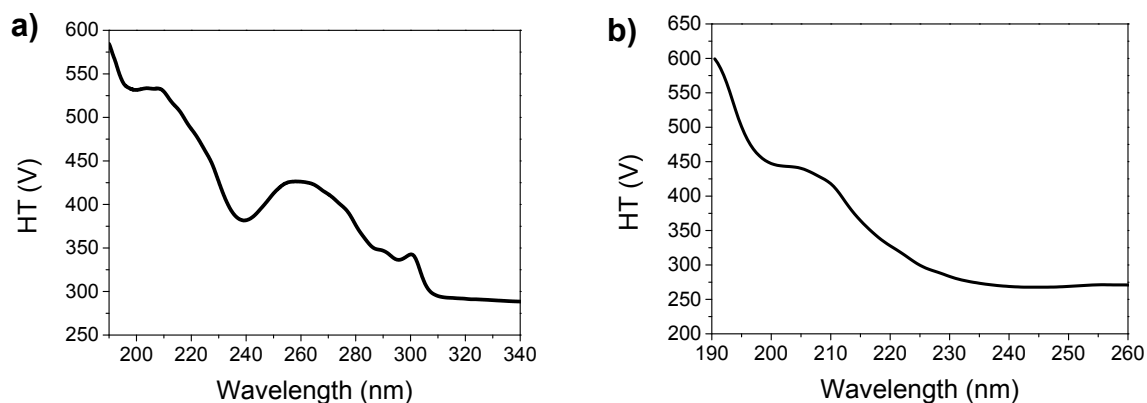
<sup>b</sup> State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, PR China.

<sup>c</sup> Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin, 300072, PR China

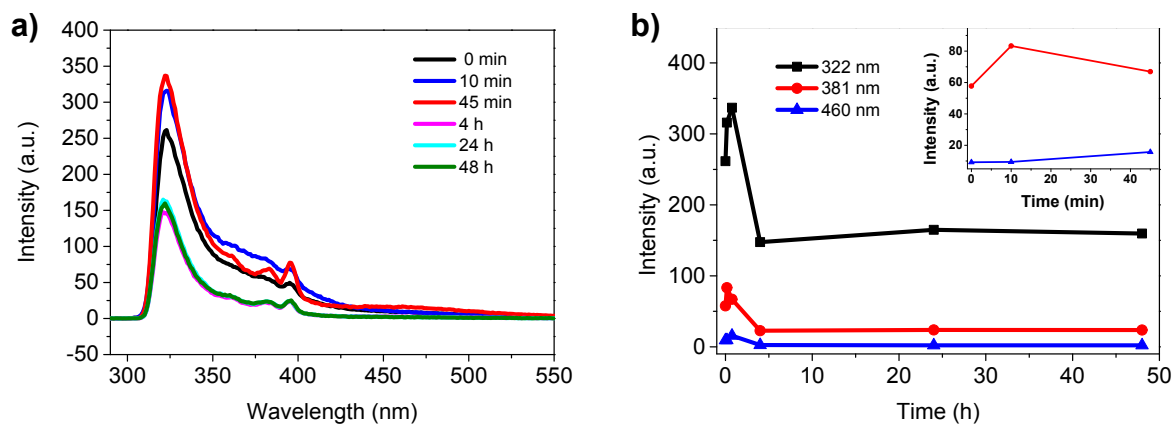
<sup>d</sup> The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, PR China

**E-mail:** tjurl@tju.edu.cn (R. H.); qiwei@tju.edu.cn (W. Q.); Tel: +86 22 27407799

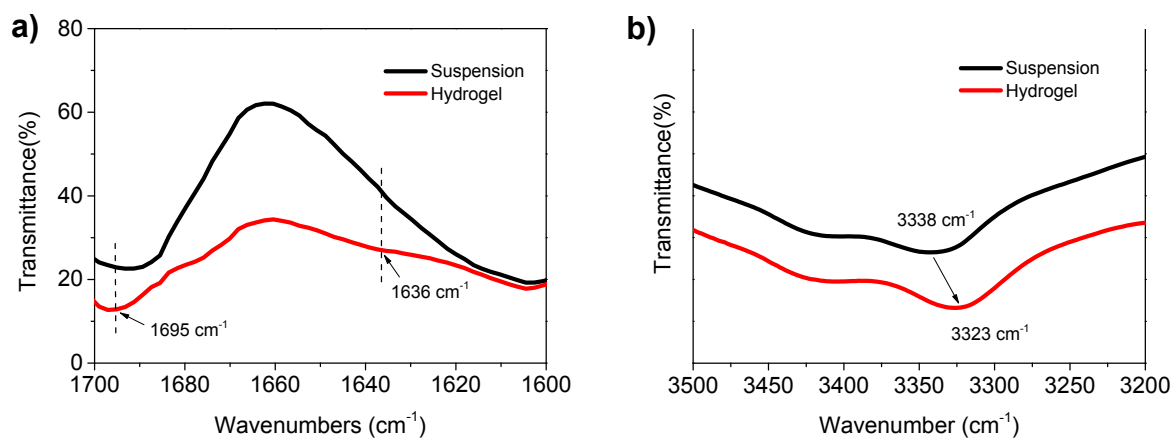
## Supplementary Figures



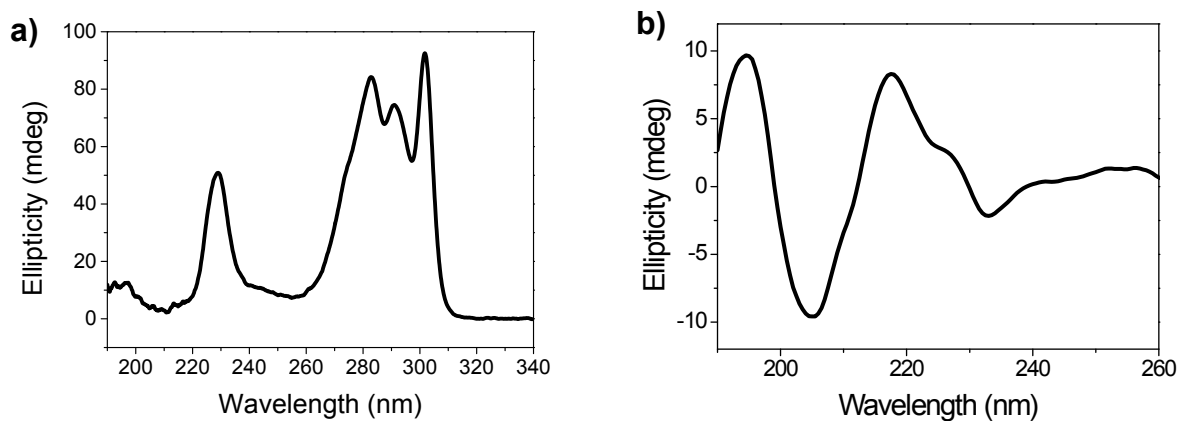
**Figure S1** a) HT spectrum of the hydrogel formed from Fmoc-F and F-OMe with  $\alpha$ -chymotrypsin loading of 0.5 mg mL<sup>-1</sup>. b) HT spectrum of the hydrogel after washing with deionized water for three times.



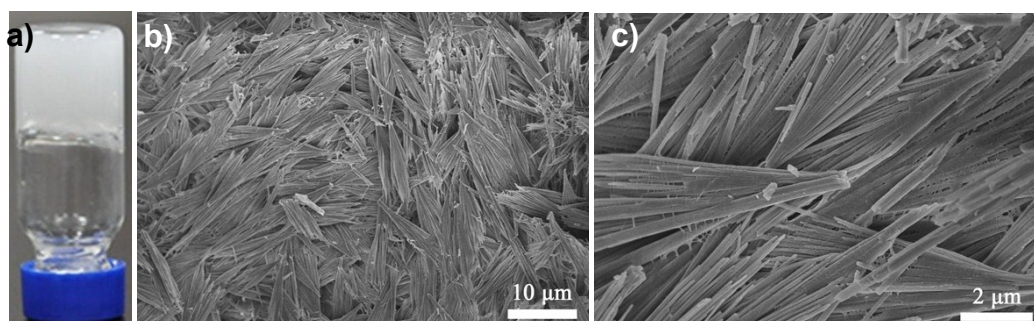
**Figure S2** a) Fluorescence emission spectra of the Fmoc-F/F-OEt hydrogel monitored over 48 h. b) Fluorescence intensity of the peaks at 322 nm, 381 nm and 460 nm within fluorescence spectra monitored with time. The inset in Figure S1b shows the relative fluorescence intensity of peaks at 395 nm and 460 nm within 45 minutes.



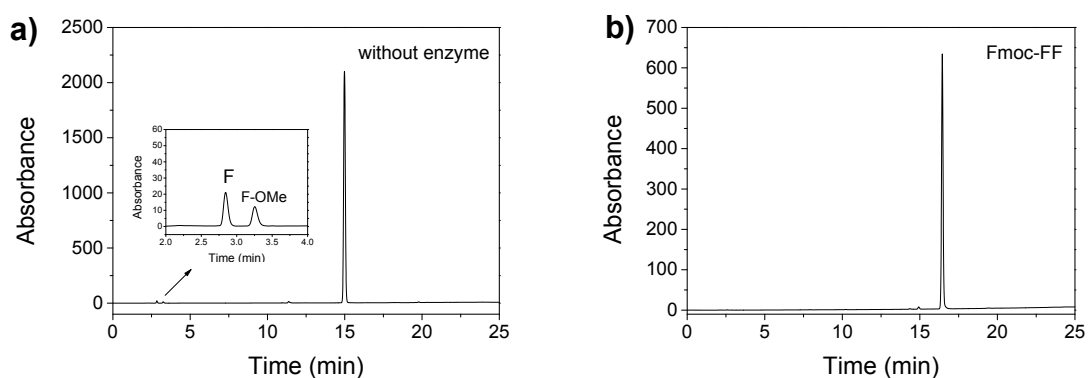
**Figure S3** a) Amide I region of FTIR absorbance spectra of the Fmoc-F/F-OEt hydrogel, representing carbonyl stretching mode of amino acid residues. b) FTIR absorbance spectra of the Fmoc-F/F-OEt hydrogel between 3200~3500 cm<sup>-1</sup>, representing the change in N-H stretching bands.



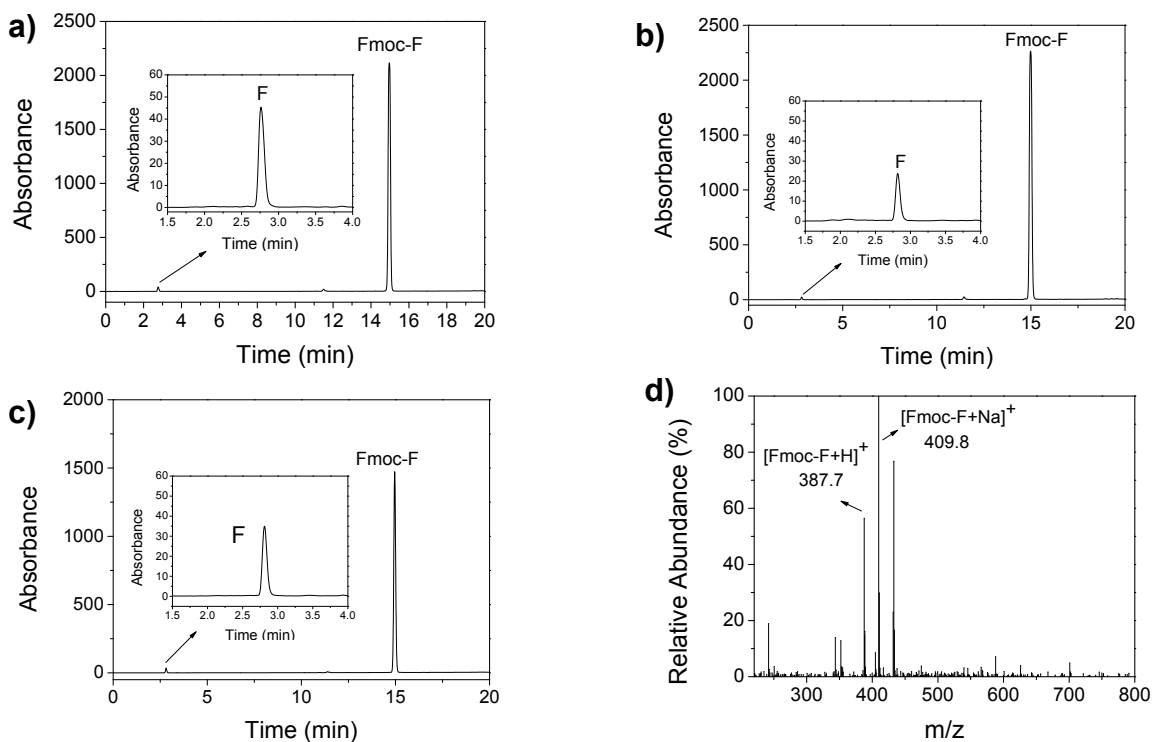
**Figure S4** a) CD spectrum of the Fmoc-F/F-OEt hydrogel at  $\alpha$ -chymotrypsin loading of  $0.5 \text{ mg mL}^{-1}$ . b) CD spectrum of the hydrogel after washing with deionized water for three times.



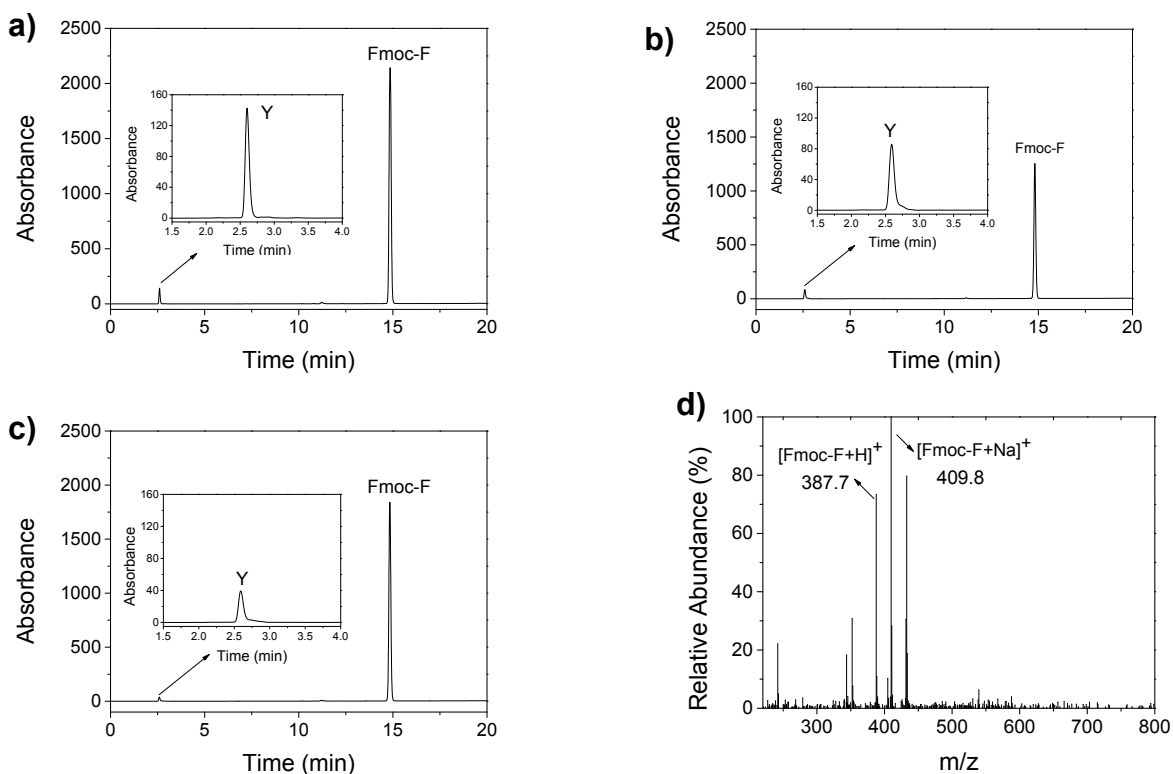
**Figure S5** a) Photographs of hydrogels formed from Fmoc-F and Y-OMe and aged for 20 min. b-c) SEM images of white precipitate in hydrogel.



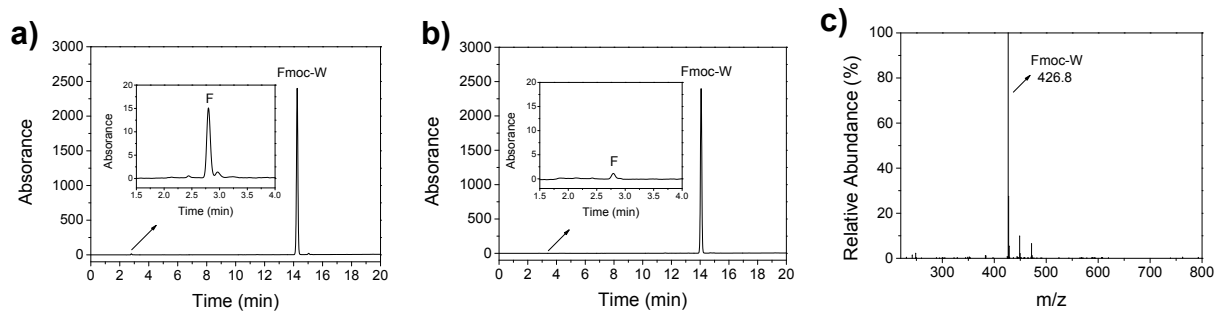
**Figure S6** a) HPLC chromatogram of Fmoc-F/F-OMe milky suspension after incubation for 24 h without addition of  $\alpha$ -chymotrypsin. b) HPLC chromatogram of Fmoc-FF.



**Figure S7** a-c) HPLC chromatograms of the Fmoc-F/F-OEt hydrogels before (a) and after (b) washing with deionized water for four times and the supernatant (c). d) Mass spectra of nanofibers after washing with deionized water.



**Figure S8** a-c) HPLC chromatograms of the Fmoc-F/Y-OMe hydrogels before (a) and after (b) washing with deionized water for four times and the supernatant (c). d) Mass spectra of nanofibers after washing with deionized water.



**Figure S9** a-b) HPLC chromatograms of the Fmoc-W/F-OMe hydrogels before (a) and after (b) washing with deionized water for 4 times. c) Mass spectra of nanofibers after washing with deionized water.



**Figure S10** Photographs of mixture of Fmoc-F, F-OH, methanol and  $\alpha$ -chymotrypsin.

## Supplementary Tables

**Table S1** Molar ratio of Fmoc-F and F or Y for the hydrogel after washing with deionized water

<b>Self-assembly system</b>	<b>Molar ratio</b>	<b>Nanofiber</b>	<b>Supernatant</b>	<b>Total</b>
<b>Fmoc-F/F-OMe</b>	Fmoc-F/F	4.346	0.718	1.023
<b>Fmoc-F/F-OEt</b>	Fmoc-F/F	2.527	0.735	1.081
<b>Fmoc-F/Y-OMe</b>	Fmoc-F/Y	0.548	2.27	1.027