Preparation of novel porphyrin nanomaterials based on the pH-responsive shape evolution of porphyrin microspheres

Wenbo Zhang[1](11229034), Lingbo Xing[1], Haisheng Wang[1], Xiujun Liu[2],Yaqing Feng[2] and Changyou Gao[1]*

1.MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
2.School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
**E-mail address: cygao@zju.edu.cn*

Introduction

Environmental-responsive self-assembly has been widely researched recently, which can change the shape or properties of the materials. However, stimuli-triggered shape evolutions of organic microspheres have rarely been reported so far. Here a novel kind of porphyrin microspheres (PAH-g-Por MPs) were prepared. The PAH-g-Por MPs transformed into four different kinds of novel one-dimensional self-assembly structures (NRs@pH1, NRs@pH2, NRs@pH3 and WSs@pH4) after incubation in pH1, pH2, pH3 and pH4 hydrochloric acid, respectively. The rate and degree of hydrolysis had an important effect on formation of the three structures. The MPs and the four self-assembled structures emitted stable red fluorescence, which will find potential applications in different fields.

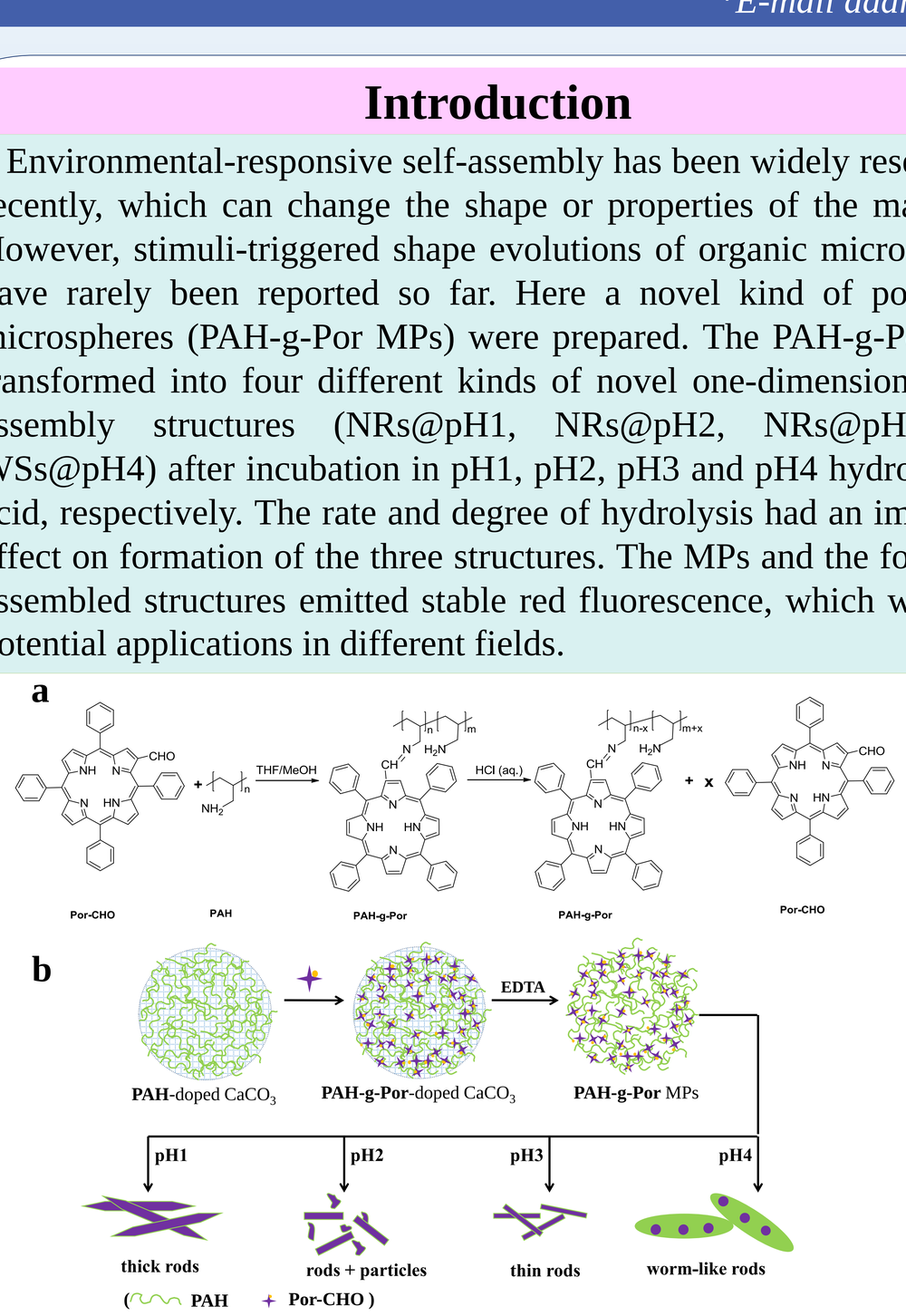

Figure 1. (a) Schematic illustration of formation and decomposition of PAH-g-Por; (b) Structure evolution and formation of various nano-structures of PAH-g-Por microspheres at different pH values.

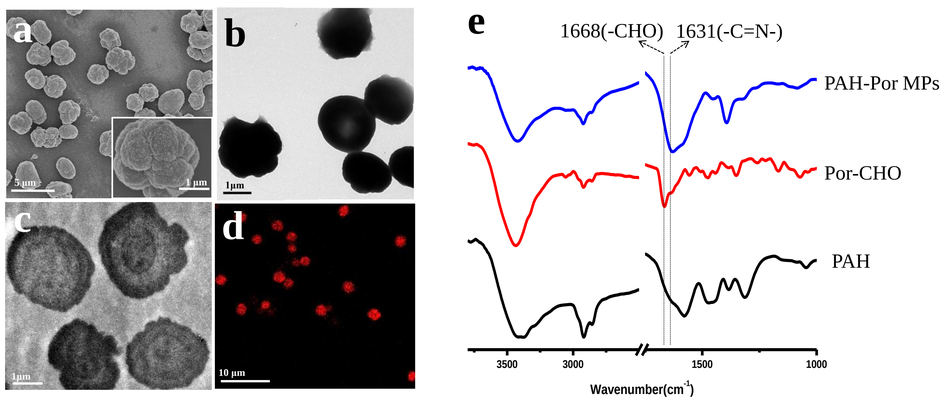

Figure 2. (a) SEM (inset, higher magnification), (b) TEM, (c) cross section (ultramicrotomy) TEM and (d) CLSM images of PAH-g-Por microspheres. (e) FTIR spectra of Por-CHO, PAH, and PAH-g-Por MPs.

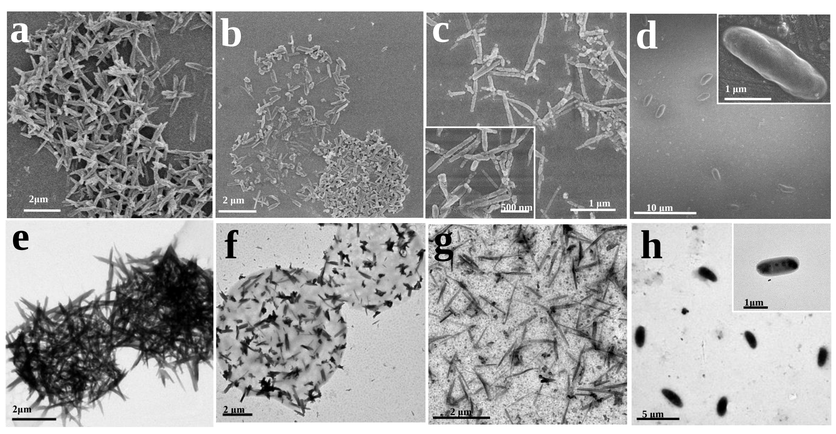

Figure 3. (a-d) SEM and (e-h) TEM images (inset, higher magnification) of decomposition-assembly structures of PAH-g-Por MPs after treatment in (a,e) pH 1, (b,f) pH 2, (c,g) pH 3 and (d,h) pH 4 HCl for 7 d, 7d, 30d and 40 d, respectively .

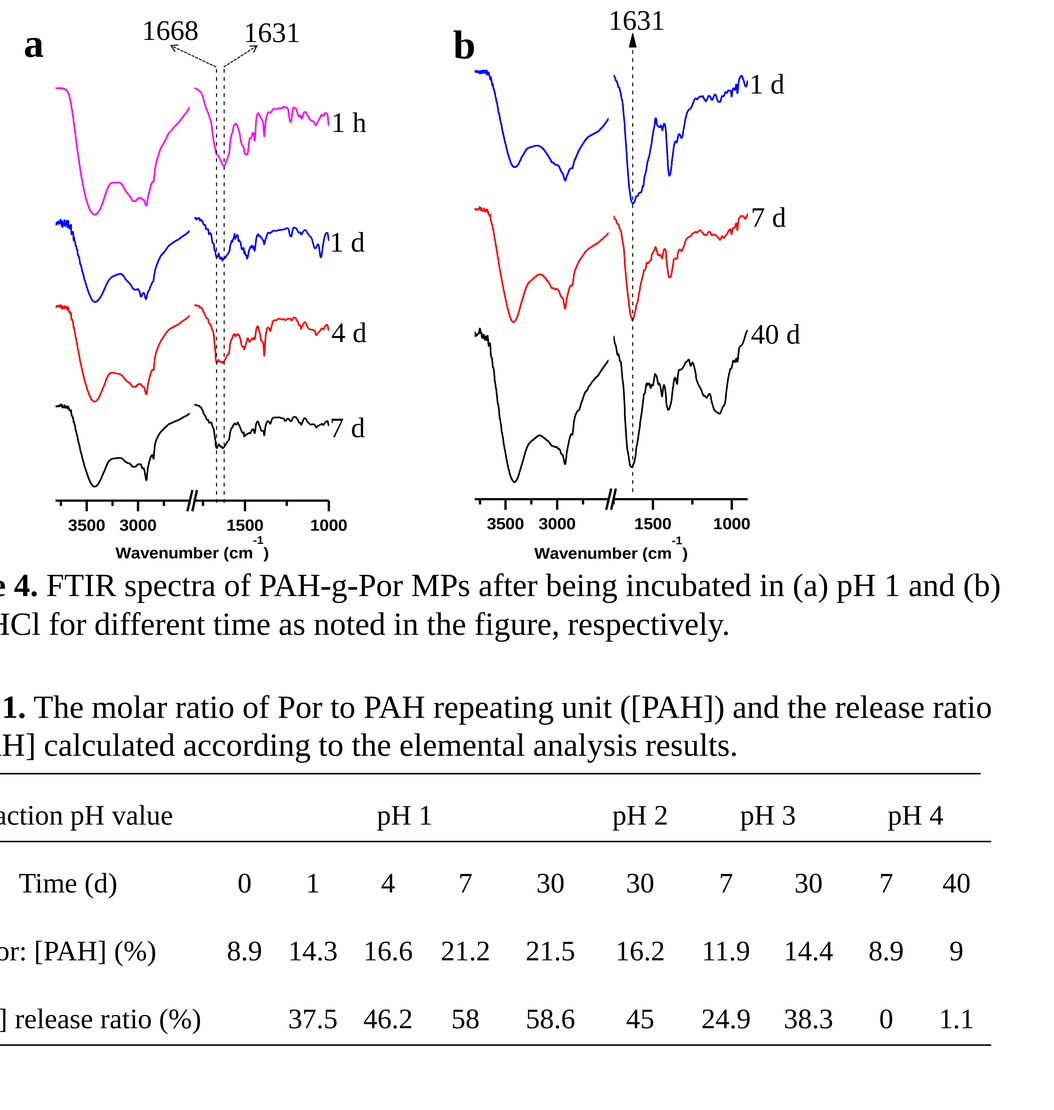

Figure 4. FTIR spectra of PAH-g-Por MPs after being incubated in (a) pH 1 and (b) pH 4 HCl for different time as noted in the figure, respectively.

Table 1. The molar ratio of Por to PAH repeating unit ([PAH]) and the release ratio of [PAH] calculated according to the elemental analysis results.

Reaction pH value	pH 1					pH 2	pH 3		pH 4	
Time (d)	0	1	4	7	30	30	7	30	7	40
Por: [PAH] (%)	8.9	14.3	16.6	21.2	21.5	16.2	11.9	14.4	8.9	9
[PAH] release ratio (%)		37.5	46.2	58	58.6	45	24.9	38.3	0	1.1

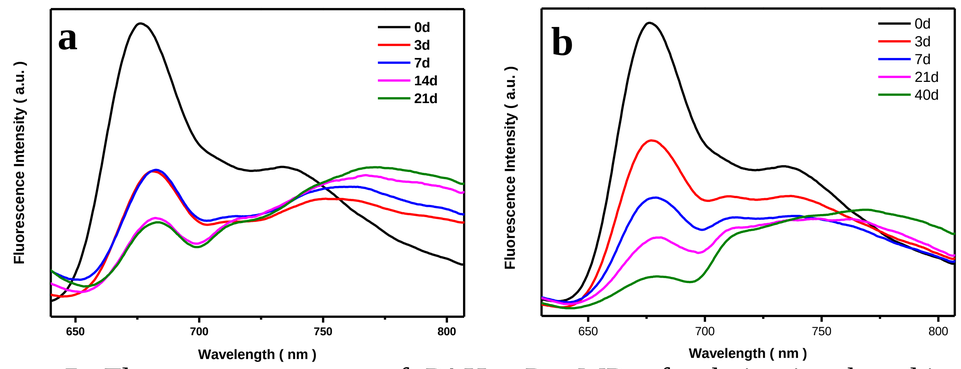

Figure 5. Fluorescence spectra of PAH-g-Por MPs after being incubated in (a) pH 1 and (b) pH 4 HCl for different time as noted in the figure, respectively. The excitation wavelength is 420 nm.

Conclusion

The pH-responsive decomposition-assembly of PAH-g-Por MPs leads to four kinds of novel porphyrin nanomaterials, which haven't been reported for Por-CHO. The rate and degree of Schiff base hydrolysis have an important effect on the formation of the four structures. NRs@pH1, NRs@pH2 and NRs@pH3 are all composed of the released Por-CHO and the unhydrolyzed PAH-g-Por due to the partial hydrolysis of the Schiff base. At pH4, the PAH-g-Por MPs undergo a shape evolution process without hydrolysis to produce WSs@pH4.

Acknowledgements

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References

[1] Z. P. Wang, H. Moehwald, C. Y. Gao. Nanotubes Protruding from Poly(allylamine hydrochloride)-Graft-Pyrene Microcapsules. ACS Nano. 2011, 5: 3930–3936.