## Two dimensional supramolecular assemblies from pH responsive poly(ethyl glycol)-*b*poly(L-glutamic acid)-*b*-poly(N-octylglycine) triblock copolymer

Yunxia Ni<sup>1</sup>, Jing Sun<sup>1</sup>\*, Yuhan Wei<sup>1</sup>, Xiaohui Fu<sup>1</sup>, Chenhui Zhu<sup>2</sup>, Zhibo Li<sup>1</sup>\*

<sup>1</sup>Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department; School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

<sup>2</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley,

California 94720, United States



Scheme S1. Synthetic routes of (a) Oct-NNCA and (b) PEG-b-PGA-b-PNOG.



**Figure S1.** <sup>1</sup>H NMR of (a) BLG-NCA (500 MHz,  $CDCl_3$ ,  $\delta$ , ppm): 1.86-2.12 (m, 2H), 2.52 (t, 2H), 4.47 (t, 2H), 5.09 (s, 2H), 7.31-7.36 (m, 5H) and (b) Oct-NNCA (500 MHz,  $CDCl_3$ ,  $\delta$ , ppm): 0.90 (t, 3H), 1.28-1.32 (m, 10H), 1.60-1.64 (m, 2H), 3.41 (t, 2H), 4.10 (s, 2H). \* indicates  $CDCl_3$ .



Figure S2. FTIR spectrums of BLG-NCA, Oct-NNCA, PEG-*b*-PBLG and PEG-*b*-PBLG-*b*-PNOG.



**Figure S3.** Representative GPC chromatograms of (a) PEG-*b*-PBLG<sub>64</sub> and PEG-*b*-PBLG<sub>64</sub>-*b*-PNOG<sub>21</sub>; (b) PEG-*b*-PBLG<sub>24</sub> and PEG-*b*-PBLG<sub>24</sub>-*b*-PNOG<sub>17</sub>; (c) PEG-*b*-PBLG<sub>24</sub> and PEG-*b*-PBLG<sub>24</sub>-*b*-PNOG<sub>11</sub>.



**Figure S4.** The DSC thermograms of all the triblock copolymers: black curve represents PEG-*b*-PGA<sub>64</sub>-*b*-PNOG<sub>21</sub>; pink curve represents PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>11</sub>; blue curve represents PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>17</sub>; red curve represents PEG-*b*-PGA<sub>42</sub>-*b*-PNOG<sub>17</sub>.



**Figure S5.** CD spectrum of (a) PEG-*b*-PGA<sub>64</sub>-*b*-PNOG<sub>21</sub>; (b) PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>17</sub>; (c) PEG*b*-PGA<sub>24</sub>-*b*-PNOG<sub>11</sub> at different pH.



**Figure S6**. Cryo-TEM micrographs of (freshly prepared) 0.2 wt % PEG-*b*-PGA<sub>42</sub>-*b*-PNOG<sub>17</sub> in aqueous solution at (a) pH 7.2 and (b) pH 4.8. The arrows indicate the self-assemblies that lie orthogonal to the plane.



Figure S7. TEM image of PEG-*b*-PGA<sub>42</sub>-*b*-PNOG<sub>17</sub> at pH 2.5 at concentration of 2 mg/mL.



**Figure S8.** AFM image of (a)  $PEG-b-PGA_{64}-b-PNOG_{21}$  at pH 4.8 and (b)  $PEG-b-PGA_{24}-b-PNOG_{17}$  at pH 7.2 at concentration of 2 mg/mL.



**Figure S9.** (a) TEM image and (b) AFM image of PEG-*b*-PGA<sub>64</sub>-*b*-PNOG<sub>21</sub> at pH 7.2 at concentration of 2 mg/mL. (c) TEM image and (d) AFM image of PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>17</sub> at pH 4.8 at concentration of 2 mg/mL.



**Figure S10.** TEM image of PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>11</sub> at (a) pH 7.2 and (c) pH 4.8 at concentration of 2 mg/mL; AFM image of PEG-*b*-PGA<sub>24</sub>-*b*-PNOG<sub>11</sub> at (b) pH 7.2 and (d) pH 4.8 at concentration of 2 mg/mL.

Samples	Structure Type		Height (nm)	
	pH 7.2	pH 4.8	pH 7.2	pH 4.8
PEG-b-PBLG <sub>64</sub> -b-PNOG <sub>21</sub>	disk	disk	5.2±0.4	9.8±0.6
PEG-b-PBLG <sub>42</sub> -b-PNOG <sub>17</sub>	disk	sheet	5.9±0.4	10.2±0.4
PEG-b-PBLG <sub>24</sub> -b-PNOG <sub>17</sub>	sheet	sheet	9.2±0.6	9.8±0.6
PEG-b-PBLG <sub>24</sub> -b-PNOG <sub>11</sub>	disk	sheet	6.0±0.3	8.0±0.5

Table S1. The characteristics of the assembles of all the triblock copolymers at different pH.

\*For statistical analysis, ~ 40 nanodisks or nanosheets were traced to determine the size.