Electronic Supplementary Information (ESI) for

Twin-tailed Tadpole-Shaped Amphiphilic Copolymer of Poly(ethylene glycol) and Cyclic Poly(ε-caprolactone): Synthesis, Self-assembly and Biomedical Application

Yanyan Zhou[1], Lei Li[1], Wei Chen[1], Dian Li[1], Nianchen Zhou[1], Jinlin He[1],* Peihong Ni[1], Zhengbiao Zhang[1,]* and Xiulin Zhu[1,2]

[1] State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

[2] Global Institute of Software Technology, No 5. Qingshan Road, Suzhou National Hi-Tech District, Suzhou 215163, China.

E-mail: jlhe@suda.edu.cn (J. He); zhangzhengbiao@suda.edu.cn (Z. Zhang)

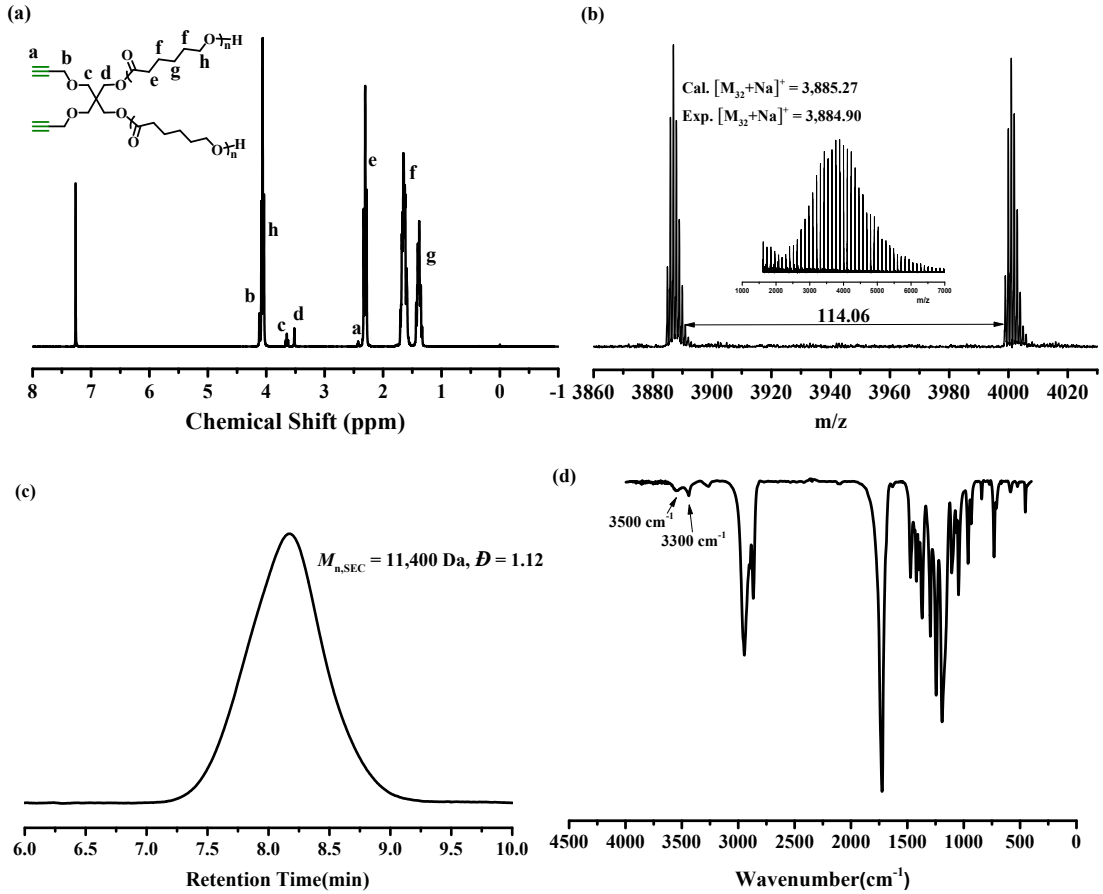

Figure S1. Structural characterizations of 2alkynyl-*l*-PCL-2OH: (a) ^{1}H NMR spectrum in $CDCl_3$, (b) MALDI-TOF mass spectrum, (c) SEC trace, and (d) FT-IR spectrum.

PCL with two alkynyl end groups was prepared by ring opening polymerization of ε-CL from functionalized initiator 2, 2-bis((prop-2-yn-1-yloxy)methyl)propane-1, 3-diol. The polymer was characterized by MALDI-TOF MS, SEC, FT-IR and ^{1}H NMR. Based on the integral ratio of peak "c" corresponding to methylene group of the initiator and peak "g" corresponding to methylene groups of PCL chain in ^{1}H NMR spectrum shown in Figure S1a, the molecular weight ($\bar{M}_{n,\ NMR}$) is calculated to be 7,200 Da. The MALDI-TOF mass spectrum of 2alkynyl-*l*-PCL-2OH is shown in Figure S1b. Only one single symmetric distribution of molecular weights is observed where the monoisotopic mass of each peak matches well with that expected for the proposed structure (Cal. $[M+Na]^+$: 3885.27 Da, Exp. $[M+Na]^+$: 3384.90 Da). The mass gap between two neighboring peaks agrees well with the mass of one PCL repeating unit (114.07 Da). SEC trace of 2alkynyl-*l*-PCL-2OH is shown in Figure S1c, confirming the unimodal distribution linear PCL. From the FT-IR spectrum (Figure S1d), one can

clearly observe the characteristic vibrational bands of hydroxyl group around 3,500 cm^{-1} and the alkynyl group around 3,300 cm^{-1}. All these data confirm the precisely-defined structure and molecular homogeneity of 2alkynyl-*l*-PCL-2OH.

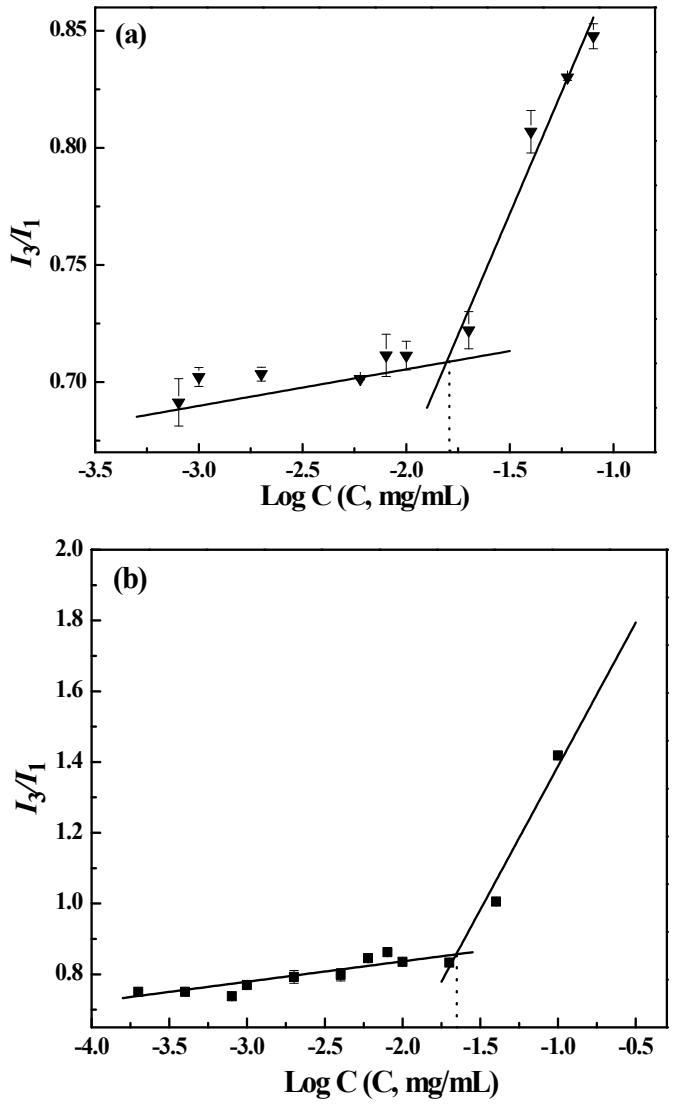

Figure S2. Intensity ratios (I_3/I_1) in fluorescence emission spectra of pyrene as a function of the logarithm concentrations of (a) PEG-*b*-(*c*-PCL)-*b*-PEG and (b) PEG-*b*-(*l*-PCL)-*b*-PEG.