## **Supplementary Materials**

## Well-defined Podophyllotoxin Polyprodrug Brush: Preparation via RAFT Polymerization and Evaluation as Drug Carrier

Yifei Guo,<sup>†</sup> Chunying Hao,<sup>†</sup> Xiangkang Wang,<sup>‡</sup> Yanna Zhao,<sup>†</sup> Meihua Han,<sup>†</sup> Mincan Wang,<sup>\*,‡</sup> Xiangtao Wang<sup>\*,†</sup>

 Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences & Peking Union Medical College, No. 151, Malianwa North Road, Haidian District, Beijing 100193, China

<sup>‡</sup> The College of Chemistry and Molecular Engineering, Zhengzhou University, No. 75 Daxue Road, Zhengzhou, Henan 450052, P. R. China

E-mail: xtaowang@163.com; Fax: +86 10 57833266; Tel: +86 10 57833264



Figure S1. <sup>1</sup>H NMR spectrum of chain transfer agent CTA.



**Figure S2.** <sup>1</sup>H NMR spectrum of podophyllotoxin methacrylate monomer.



Figure S3. <sup>1</sup>H NMR spectrum of triethylene glycol methacrylate monomer.



**Figure S4.** <sup>1</sup>H NMR spectrum of poly(triethylene glycol methacrylate).



Figure S5. <sup>1</sup>H NMR spectrum of polyprodrug brush PT<sub>35</sub>P<sub>2</sub>.



Figure S6. <sup>1</sup>H NMR spectrum of polyprodrug brush PT<sub>35</sub>P<sub>6</sub>.



Figure S7. <sup>1</sup>H NMR spectrum of polyprodrug brush PT<sub>35</sub>P<sub>22</sub>.



Figure S8. <sup>1</sup>H NMR spectrum of polyprodrug brush PT<sub>35</sub>P<sub>39</sub>.



Figure S9. DLS curves of polyprodrug brushes in aqueous solution.

Table S1. Conditions for and results of a series of polyprodrug brush PTP

Entries	DP a	r <sup>b</sup>	Conv. <sup>c</sup>	Mn, <sub>theor.</sub> d
			(%)	(×10 <sup>-4</sup> )
PT <sub>35</sub>	45 <sup>e</sup>	-	45	1.11
PT <sub>35</sub> P <sub>2</sub>	3 <sup>f</sup>	1:0.1	60	1.25
PT <sub>35</sub> P <sub>6</sub>	8	1:0.2	80	1.50
PT <sub>35</sub> P <sub>11</sub>	14	1:0.3	56	1.78
PT <sub>35</sub> P <sub>22</sub>	28	1:0.5	56	2.46
PT <sub>35</sub> P <sub>39</sub>	50	1:1.0	53	3.52

<sup>a</sup> Degree of polymerization. <sup>b</sup> Block ratios, calculated from DP. <sup>c</sup> Convesion. <sup>d</sup> Theoretical molar mass.