Supplementary Information

## Hydrogen peroxide-responsive anticancer hyperbranched polymer micelles for enhanced cell apoptosis

Bing Liu,<sup>‡a</sup> Dali Wang,<sup>‡b</sup> Yakun Liu,<sup>a</sup> Qian Zhang,<sup>a</sup> Lili Meng,<sup>b</sup> Huirong Chi,<sup>a</sup> Jinna

Shi,<sup>c</sup> Guolin Li,<sup>\*,a</sup> Jichen Li,<sup>\*,a</sup> and Xinyuan Zhu<sup>\*,b</sup>

<sup>a</sup> Department of Oral and Maxillofacial Surgery, The First Affiliated Hospital of

Harbin Medical University, 23 Youzheng Street, Nangang District, Harbin 150001,

People's Republic of China

<sup>b</sup> School of Chemistry and Chemical Engineering, State Key Laboratory of Metal

Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

<sup>c</sup> Department of Periodontology, The First Affiliated Hospital of Harbin Medical University, 23 Youzheng Street, Nangang District, Harbin 150001, People's Republic

of China

<sup>+</sup> These authors are joint first authors.



*Figure S1.* <sup>1</sup>H NMR spectrum of HPG in DMSO-*d*<sub>6</sub> (400 MHz, 298 K).



*Figure S2.* <sup>1</sup>H NMR spectrum of acryloyl-terminated HPG in DMSO- $d_6$  (400 MHz, 298 K).



Figure S3. Representative DSC curves of HPG and HPG-2S-SN38.



Figure S4. The TEM image of the CA-loaded HPG-2S-SN38 micelles.



*Figure S5.* The HPLC traces of HPG-2S-SN38 micelles treated with 1 mM  $H_2O_2$  for 12 h. The peak at 3.60 min was SN38 derived from the thiolysis of HPG-2S-SN38.



*Figure S6.* Mass spectrum (ES+) of SN38 released from HPG-2S-SN38 micelles treated with 5 mM  $H_2O_2$  for 12 h. (M+H<sup>+</sup>, m/z = 393.1440)



*Figure S7. In vitro* release of nile red from HPG-2S-SN38 micelles in PBS (pH 7.4, 50 mM) at 37 °C with or without treatment of 1 mM  $H_2O_2$ . Data are presented as the average  $\pm$  standard deviation (n = 3).



*Figure S8.* Representative confocal laser scanning microscopy images of MCF-7 cells incubated with nile red-loaded HPG-2S-SN38 micelles for 2 h. Scale bar: 20 μm.



*Figure S9.* Cell viability of MCF-7 cells against HPG after cultured for 48 h with different concentrations.



*Figure S10.* Cell viability of L929 cells (mouse fibroblast cells) against CA-loaded HPG-2S-SN38 after cultured for 48 h with different concentrations.