Supporting Information for

Reactive Oxygen Species (ROS)-Responsive Tellurium-Containing Hyperbranched Polymer

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1. Materials

Tellurium powder, sodium borohydride, NaH, 1,3,5tris(bromomethyl)benzene and 11-bromoundecan-1-ol was purchased from J&K Scientific Company. Methoxypolyethylene glycols $(M_n=1900)$, was purchased from Sigma-Aldrich. Vitamin C (VC) was purchased from Alfa Aesar.

2. Instruments

¹H-NMR spectra : ¹H-NMR spectra was recorded on a JOEL JNM—ECA400 apparatus (400 MHz).

Gel permeation chromatography (GPC) measurement was performed on a Agilent LC 1260 with a MWD detecter, using polystyrene as a standard and DMF as eluent.

Dynamic light scattering (DLS) measurement: DLS data was obtained on a Malvern Zetasizer Nano ZS90 using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90° at 25 °C.

Transmission electron microscopy (TEM) images were obtained from a JEM-2010 Microscope with an accelerating voltage of 120 kV, and the samples were prepared by drop-coating the aqueous solution on the carbon-coated copper grid for 15 min and observed without staining.

Atomic emission spectroscopy (AES) experiment was performed on an X Series ICP-MS (Thermo Electron Co., Winsford, Cheshire, UK). The sample was made by solving the powder of polymer in water.

X-ray photoelectron spectroscopy (XPS) analysis: Performed on a PHI Quantera scanning X-ray microprobe. XPS sample preparation: Each compound was solubilized by water, this solution was dropped onto a piece of silicon, then the solvent was pumped away in vacuum, finally, a film of the compound on silicon was obtained to carry out XPS measurement.

Fourier transform infrared spectroscopy (FTIR) spectroscopy: Spectra were obtained from a Perkin–Elmer Spectrum One spectrophotometer (room temperature). The spectra were obtained by collecting 32 scans with a spectral resolution of 4 cm⁻¹ between 400 and 4000 cm⁻¹.

3. Synthetic procedure (Scheme 2 in main text)

1.1 The synthetic procedure of 11,11'-tellurobis(undecan-1-ol) was according to our previous work^{S1}. 132.4 mg tellurium (1.04 mmol) and 84 mg NaBH₄ (2.22 mmol) reacted in 5 ml water for 10 min at R. T., protected by nitrogen. The obtained compound disodium telluride (about 1.04 mmol)

reacted with 11-bromoundecan-1-ol of 450mg (1.8 mmol) in THF at 50 °C. The resulting compound was dried to eliminate THF, then extracted by dichloro methane, the dichloro methane phase was collected and dried. The resulting solid was dissolved by THF, then recrystallized by petroleum ether to generate a white powder with a yield of ~60 %. ¹H-NMR (400 MHz, DMSO-d6, 298 K) δ (ppm): 4.31 (2H, t, OH), 3.33 (4H, m, HOCH₂), 2.58(4H, t, TeCH₂), 1.60-1.72 (4H, m, CH₂CH₂OH); 1.20-1.45(32H, m, HOCH₂CH₂ (CH₂)₈CH₂Te).

1.2 The synthetic procedure of HBPTe1900: as shown in scheme 2 in main text, in DMF, at R. T., protected by argon, the 11,11'-tellurobis(undecan-1-ol) reacted with NaH to generate sodium 11,11'-tellurobis(undecan-1-ol). In DMF, at R. T., methoxypolyethylene glycols $(M_n=1900)$ reacted with NaH to generate sodium methoxypolyethylene (NaO-PEG-OMe). Then, in DMF, at 70 °C, protected by argon, sodium 11,11'-tellurobis(undecan-1-ol) reacted with excess 1,3,5-tris(bromomethyl)benzene (n_{Br} : $n_{OH}=1.15$) for 3 h to generate a hyperbranched polymer with -CH₂Br as periphery. Then, NaO-PEG-OMe ($M_n=1900$) was added to generate HBPTe1900. The raw product was purified by precipitation in diethyl ether to yield a white powder. The yield is about 30%.



¹H NMR (400 MHz, DMSO-d6, 298 K) δ (ppm):7.37-8.34 (multiple, b), 4.01-5.50 (multiple, a), 3.40-3.65 (multiple, c and PEG), 3.24 (s, PEGO*CH*₃), 2.73-3.20 (multiple, g), 1.55-2.25 (multiple, d), 1.00-1.50 (multiple, e and f).

1.3 The synthetic procedure of HC-HBPTe1900 was same as the synthetic procedure of HBPTe1900 except that sodium 11,11'-tellurobis(undecan-1-ol) reacted with excess 1,3,5-tris(bromomethyl)benzene (n_{Br} : $n_{OH=}1.15$) for 8 h, instead of 3 h, to endow the final product with higher cross-linking degree.



¹H NMR (400MHz, DMSO-d6, 298 K) δ (ppm):7.44-8.36 (multiple, b), 3.99-5.44 (multiple, a), 3.40-3.65 (multiple, c and PEG), 3.24 (s, PEGO*CH*₃), 2.75-3.18 (multiple, g), 1.61-2.26 (multiple, d), 0.97-1.55 (multiple, e and f).

4. GPC for HBPTe1900 and HC-HBPTe1900.

Table S1. GPC results for molecular weights of HBPTe1900 and HC-

HBPTe1900. (Using polystyrene as a standard)

	M _n	PDI
HBPTe1900	5.0x10 ⁵	2.4
НС-НВРТе1900	9.4x10 ⁵	2.5

5. XPS for HBPTe1900.



Figure S1. XPS analysis for binding energy of Te $3d_{3/2}$ and Te $3d_{5/2}$ of HBPTe1900.

583.6 eV and 573.2 eV are the binding energy of Te $3d_{3/2}$ and Te $3d_{5/2}$ orbitals of unoxidized tellurium respectively, as confirmed by a model compound 11,11'-tellurobis(undecan-1-ol) (Fig. S3). This result indicated that the tellurium in HBPTe1900 was not oxidized.

6. Diameter change of HBPTe750 aggregates indicated by DLS.



Figure. S2 Change of the diameter of HBPTe750 aggregates over time, measured by DLS.

The stability of HBPTe750 is confirmed to be much lower than that of HBPTe1900. HBPTe750 can be oxidized by the oxygen in the air. As shown in Figure S2, 8 hours after the formation of HBPTe750 aggregates, without any H_2O_2 , it began to swell and reached a diameter twice as large as that of the beginning after 22 hours, while HBPTe1900 aggregates remained the same (Fig. 2 in the article). This difference between HBPTe750 and HBPTe1900 could result from that, the periphery PEG chains of HBPTe750 are shorter than those of HBPTe1900, thus it is easier for H_2O_2 or oxygen to attack the branched tellurium-containting parts of HBPTe750 aggregates.

7. AES data for HBPTe1900 and HC-HBPTe1900.

Table S2 AES data for Te content in HBPTe1900 and HC-HBPTe1900.

	Concentration of polymer solution (mg/mL)	Content of Te in the polymer solution (mg/L)	Weight percentage of Te in the polymer
HBPTe1900	0.71	26.02	About 3.7%
HC-HBPTe1900	0.20	6.28	About 3.2%

8. XPS for the chemical environment of tellurium in 11,11'tellurobis(undecan-1-ol)



 $HO-C_{11}H_{22}-Te-C_{11}H_{22}-OH$

Figure S3. XPS analysis for the binding energy of Te $3d_{3/2}$ and Te

3d_{5/2} of 11,11'-tellurobis(undecan-1-ol).

9. FTIR measurement for the chemical environment of tellurium in unoxidized HBPTe1900 and oxidized HBPTe1900.



Figure S4. FTIR data for unoxidized HBPTe1900 and oxidized

HBPTe1900.

10. ¹H NMR for benzene-1,3,5-triyltrimethanol (BTMOH) upon addition of H₂O₂.



Figure S5. ¹H NMR for BTMOH upon addition of H₂O₂.

We prepared a D_2O solution containing benzene-1,3,5-triyltrimethanol at 10 mM and H_2O_2 at 120 mM which was 3 times higher than the concentration of benzyl groups. After 18 hours, BTMOH did not change according to ¹H NMR results, as shown in Figure S5, this indicates that in such reacting concentrations, benzyl units were not oxidized during the reaction with H_2O_2 . In our main text, in the solution of hyperbranched polymer aggregates and H_2O_2 , the concentration of the benzyl groups on hyperbranched polymers was less than 3 mM and H_2O_2 was at 0.1 mM, the oxidation time was less than 25 hours. Integrating the above information, the benzyl groups on the hyperbranched polymers we used were not oxidized during the reaction with H_2O_2 .

11. DLS for oxidized HBPTe1900 aggregates being reduced by 100 μ M VC.

After HBPTe1900 aggregates swelled about 5 times under the stimuli of 100 μ M H₂O₂, VC was added and reached the same concentration as H₂O₂. DLS was employed to trace the size change of the aggregates. (Figure. S6)



Figure S6 Change of the diameter of oxidized HBPTe1900 aggregates being reduced by 100 μM VC, measured by DLS.

12. XPS data for HBPTe1900 (a) and HC-HBPTe1900 (b) 24 h after the addition of H₂O₂.

In Fig. S7b, the original peaks (red line) were divided by software to distinguish the peaks corresponding to unoxidized Te (pink line) and oxidized Te (blue line) respectively. As described in the main text, 583.7 eV and 573.2 eV were the binding energy of Te $3d_{3/2}$ and Te $3d_{5/2}$ orbitals of unoxidized tellurium respectively, while the peaks around 576.0 eV and 586.0 eV were corresponding to Te $3d_{5/2}$ orbitals and Te $3d_{3/2}$ orbitals of oxidized tellurium. By calculating the integral area of each peak, which is proportional to the amounts of corresponding atoms, we concluded that the percentage of oxidized tellurium atoms in HC-HBPTe1900 was much lower than that in HBPTe1900.





Figure S7. XPS analysis for the binding energy of Te $3d_{3/2}$ and Te $3d_{5/2}$ of HBPTe1900 (a) and HC-HBPTe1900 (b) 24 h after the addition of H_2O_2 .

References:

S1. W. Cao, Y. W. Gu, M. Meineck, T. Y. Li and H. P. Xu, J. Am. Chem. Soc., 2014, 136, 5132.