Supporting information

for

Preparation of Water-soluble Hyperbranched Polyester Nanoparticles with Sulfonic Acid Functional Groups and Their Micelles Behavior, Anticoagulant Effect and Cytotoxicity

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Characterization

Figure 1S. $^{13}$C NMR spectrum of HBPE-SO$_3$ NPs in DMSO-$d_6$.

HBPE-SO$_3$ NPs: $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta=179–180$ (R$_3$C–COO–CH$_2$), 74.5 (R$_3$C–CH$_2$OCH$_2$–CH$_2$–CH$_2$–SO$_3$Na), 66.1–69.5 (R$_3$C–CH$_2$–OOC), 60.7 (R$_3$C–CH$_2$–OH), 48.8 (CR$_3$–COO–), 47.7 (OCH$_2$–CH$_2$–CH$_2$–SO$_3$), 29.1

Figure 2S. The ESI-MS of (A) HBPE and (B) HBPE-SO₃ NPs.

HBPE: 1179 (1202-Na⁺). The calculated molecular weight is 1179. The main peaks (273, 389, 505, 621, 737, 853, 969, 1085, 1201) possess a distance of 116 between the two peaks, which corresponds to the repeat unit \( M_{\text{DMPA}}-M_{\text{H}_2\text{O}} \), as the red section of illustration of Figure 2S(A).

HBPE-SO₃ NPs: 1903. The calculated molecular weight of HBPE-(SO₃)₆ is 1905. So the real molecular weight is consistent with the calculated molecular weight. It indicates that the conversion ratio from hydroxyl groups to sulfonic acid groups was 50%. The result is agreed with the datum that obtained from \(^1\text{H} \text{NMR spectrum of HBPE-SO₃ NPs.}

The main peaks (475, 588, 701, 814, 927, 1040) possess a distance of 113 between the two peaks, which corresponds to the repeat unit of the red section as the illustration of Figure 2S(B). The minor peaks possess a distance of 116 between the two peaks, which corresponds to the repeat unit \( M_{\text{DMPA}}-M_{\text{H}_2\text{O}} \), as the blue section as the illustration of Figure 2S(B).

The Self-assemble Behavior of the HBPE-SO₃ NPs. Figure 3S(A, B and C) displays the interaction configuration between two HBPE-SO₃ unimolecular micelles. The calculation results show that the total interaction energy is -302.09 kcal/mol including the electrostatic interaction energy (-243.85 kcal/mol) and the Van der Waals energy (-58.24 kcal/mol). It indicates that the interaction between the two HBPE-SO₃ unimolecular micelles is very strong. Moreover, the electrostatic
interaction is much bigger than the Van der Waals energy and dominant the binding forces between the molecules, of which the hydrogen bonding and the hydrophobic interaction are the main contributors. The chair style structure of the ligand molecule is space matchable with that of the receptor (Figure 3S(C)), thus the obvious overlaps are formed between the hydrophobic and hydrophilic parts of two different HBPE-SO$_3$ unimolecular micelles (Figure 3S(A, B)). The former bring about the strong hydrophobic interaction while the later lead to the intermolecular hydrogen bonding. One of the atom O of the sulfonic acid group of the receptor and the atom H of the hydroxy group of the ligand is linked by a relatively strong O-H$\cdots$O hydrogen bond. Another weak O-H$\cdots$O hydrogen bond is formed between the O atom of the receptor and the different hydroxy group of the ligand. The structure and the parameters are shown in Figure 4S and Table 1S, respectively. From these data, it is believed that the large micelles of HBPE-SO$_3$ are aggregated and composed of small spherical building units (unimolecular micelles) that attributed to the matchable properties of these factors that include spatial structure of molecules, hydrophobic/hydrophilic correlation, and electric charge interactions of HBPE-SO$_3$ unimolecular micelles.

Figure 3S. (A) The front view of optimal HBPE-SO$_3$—HBPE-SO$_3$ unimolecular micelles configuration. HBPE-SO$_3$ unimolecular micelles receptor is shown in CPK, HBPE-SO$_3$ NPs ligand is depicted in stick. (B) The front view of optimal HBPE-SO$_3$ NPs—HBPE-SO$_3$ unimolecular micelles configuration. The molecules of the two HBPE-SO$_3$ unimolecular micelles are depicted in stick. (C) The side view of optimal
HBPE-SO$_3$—HBPE-SO$_3$ unimolecular micelles configuration. The molecules of HBPE-SO$_3$ unimolecular micelles are also shown in stick representation. All receptor molecules are highlighted in yellow and the ligand is colored by elements.

**Figure 4S.** The O-H···O hydrogen bonds between the receptor (highlighted in yellow) and the ligand molecules.

**Table 1S.** Hydrogen bond lengths (Å) and angles (°) formed between the receptor and the ligand molecules.

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<th>X─H···Y</th>
<th>d(X─H)</th>
<th>d(H···Y)</th>
<th>d(X···Y)</th>
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