## **Supplementary Information**

## Synthesis and self-assembly of nonamphiphilic hyperbranched polyoximes

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	РВН			ТВА			LIDOY
			DMSO			DMSO	hroz
Entry	Mass	Mole	volume	Mass	Mole	Volume	Yield
	(mg)	(mmol)	(mml)	(mg)	(mmol)	(mml)	(mg)
HPOX 1	47.74	0.8/3	4	180.86	1/3	5	111.3
HPOX 2	59.68	1.0/3	5	180.86	1/3	5	128.8
HPOX 3	71.62	1.2/3	6	180.86	1/3	5	110.2
HPOX 4	89.52	1.5/3	7	180.86	1/3	5	115.0

Table S1. Preparation of HPOXs with different molar ratios of two monomers.







**Figure S2**. (A) Quantitative <sup>13</sup>C NMR spectra of HPOXs and (B) their dendritic, linear and terminal structural units to calculate DB of HPOX 2 as an example.



Figure S3. TGA curves of HPOXs with different molar feeding ratios of trialdehyde

to bis-aminooxy monomers.



Figure S4. DSC curves of HPOXs with different molar feeding ratios of trialdehyde to

bis-aminooxy monomers.



Figure S5. AFM image and section analysis of HPOX 3.



**Figure S6**. <sup>1</sup>H NMR spectra of HPOX 4 in the mixture of DMSO- $d_6$  and D<sub>2</sub>O with different D<sub>2</sub>O contents at 300 K. The volume ratios of D<sub>2</sub>O to DMSO- $d_6$  are 0.0, 0.10,

0.15, 0.25, 0.30, 0.40 and 0.50, respectively.



Figure S7. <sup>1</sup>H NMR spectrum of degradability of HPOX 4 in the mixture of

DMSO- $d_6/D_2O$  at pH 4.0 before and after degradability.

By comparison with the spectrum before degradability, the signal of oxime bonds at 8.2 ppm diminishes. Meanwhile the protons of aminooxy groups obviously increase at 9.0 ppm and the aldehyde peak appears at 10.0 ppm, confirming the hydrolysis of oxime bonds catalyzed by HCl after 4 h.