

# Supplementary Information for

## PFPE-based polymeric $^{19}\text{F}$ MRI agents: a new class of contrast agents with outstanding sensitivity

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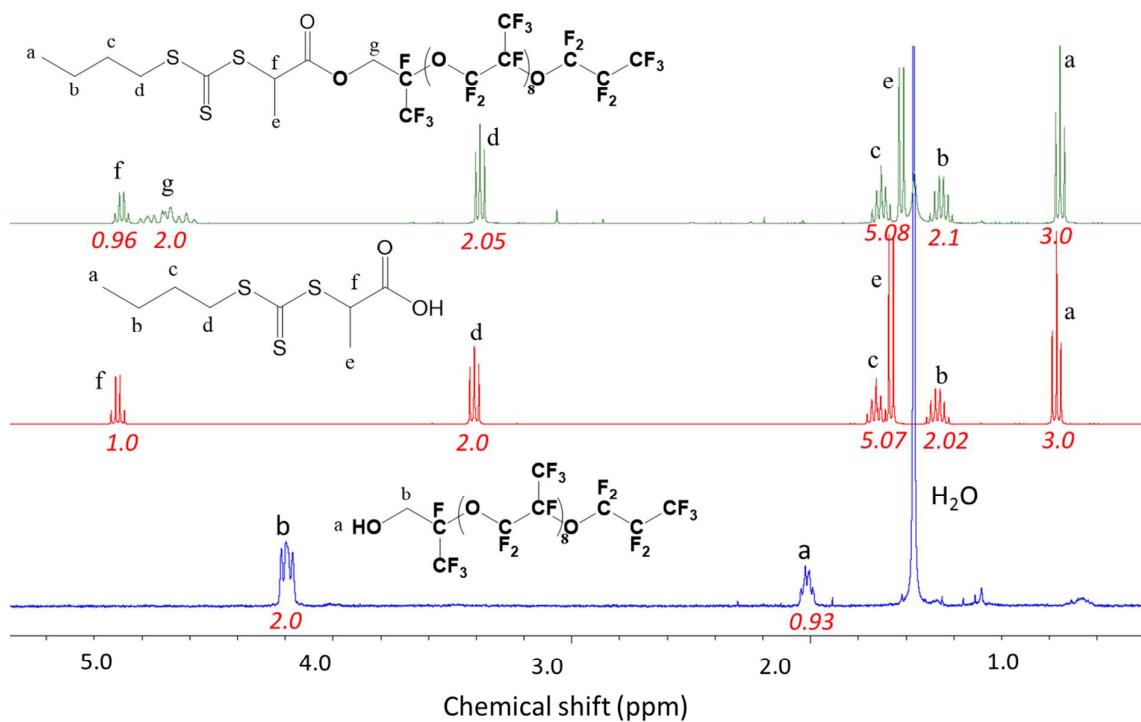
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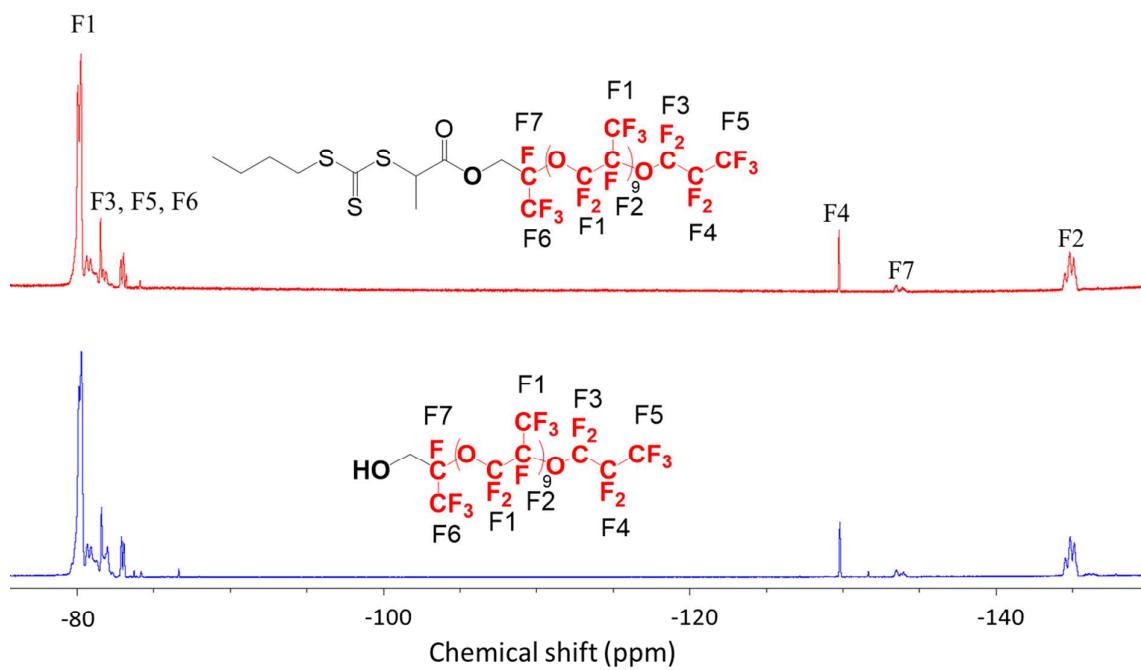
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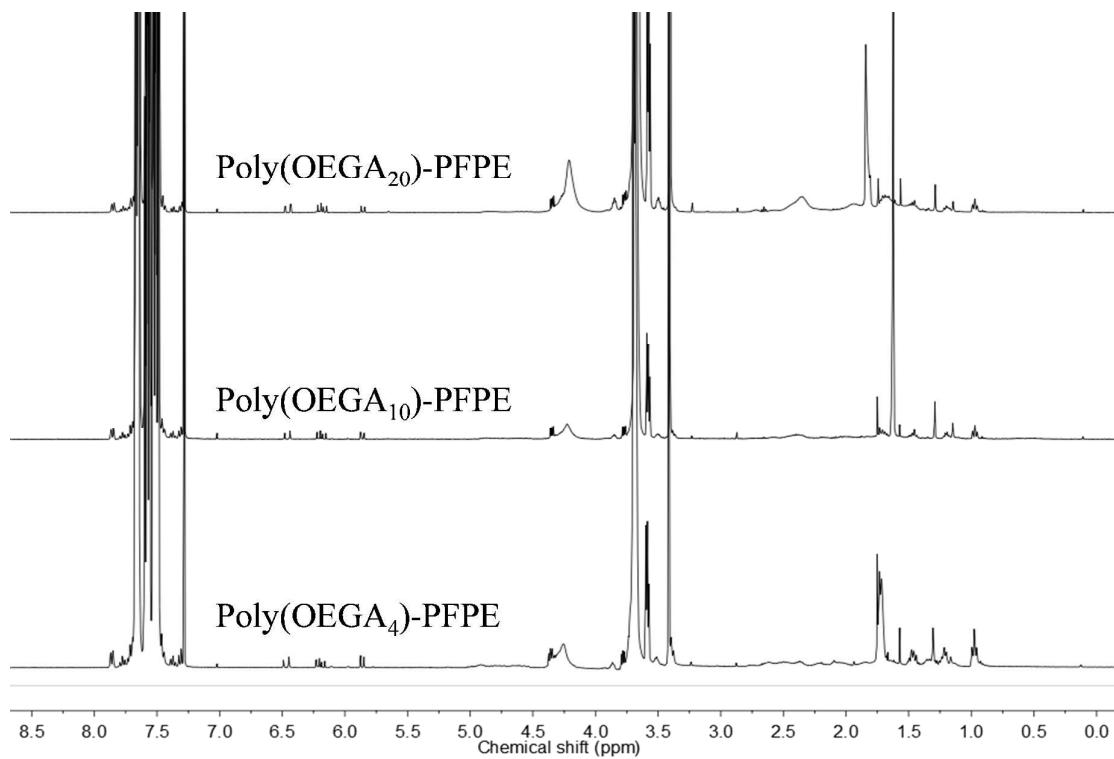
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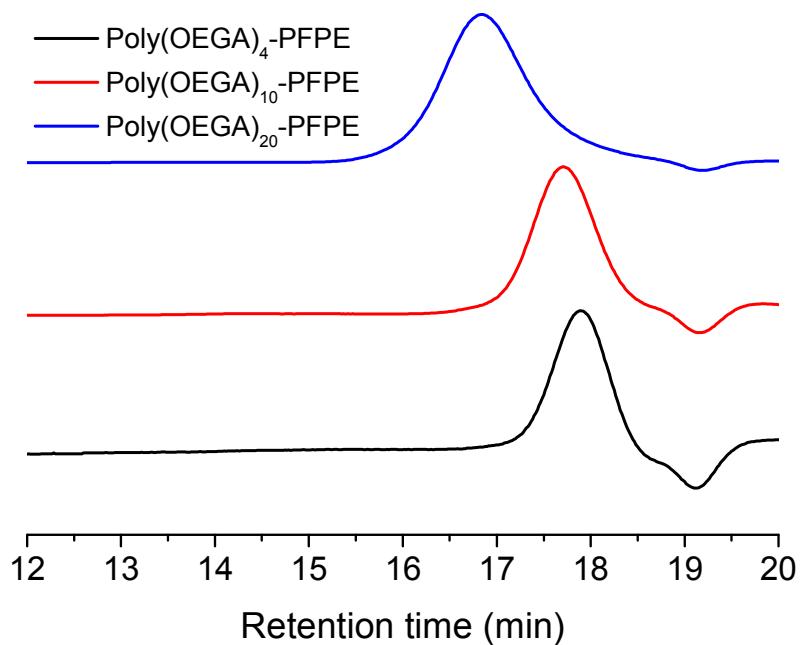
**Figure S1.** The  $^1\text{H}$  NMR spectra of PFPE-OH (bottom), PABTC (middle) and PABTC-PFPE macro-CTA (top) in  $\text{CDCl}_3$ .



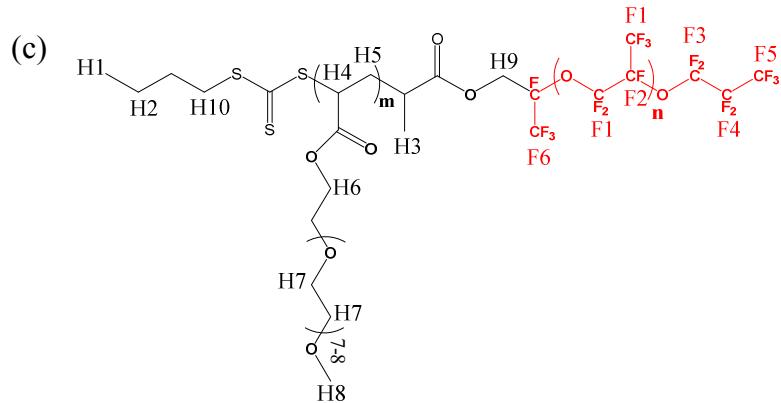
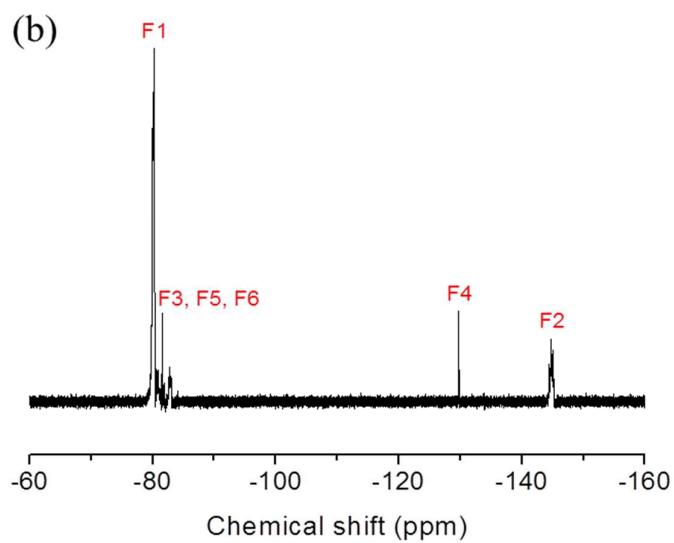
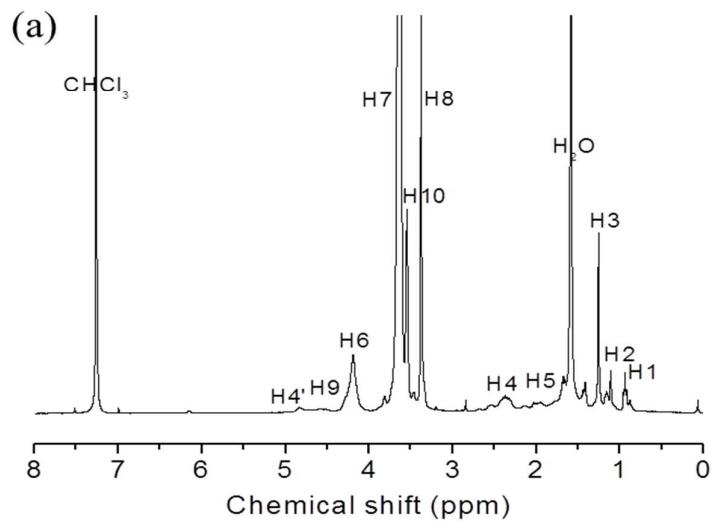
**Figure S2.** The  $^{19}\text{F}$  NMR spectrum of PFPE-OH and PABTC-PFPE macro-CTA in  $\text{CDCl}_3$ .



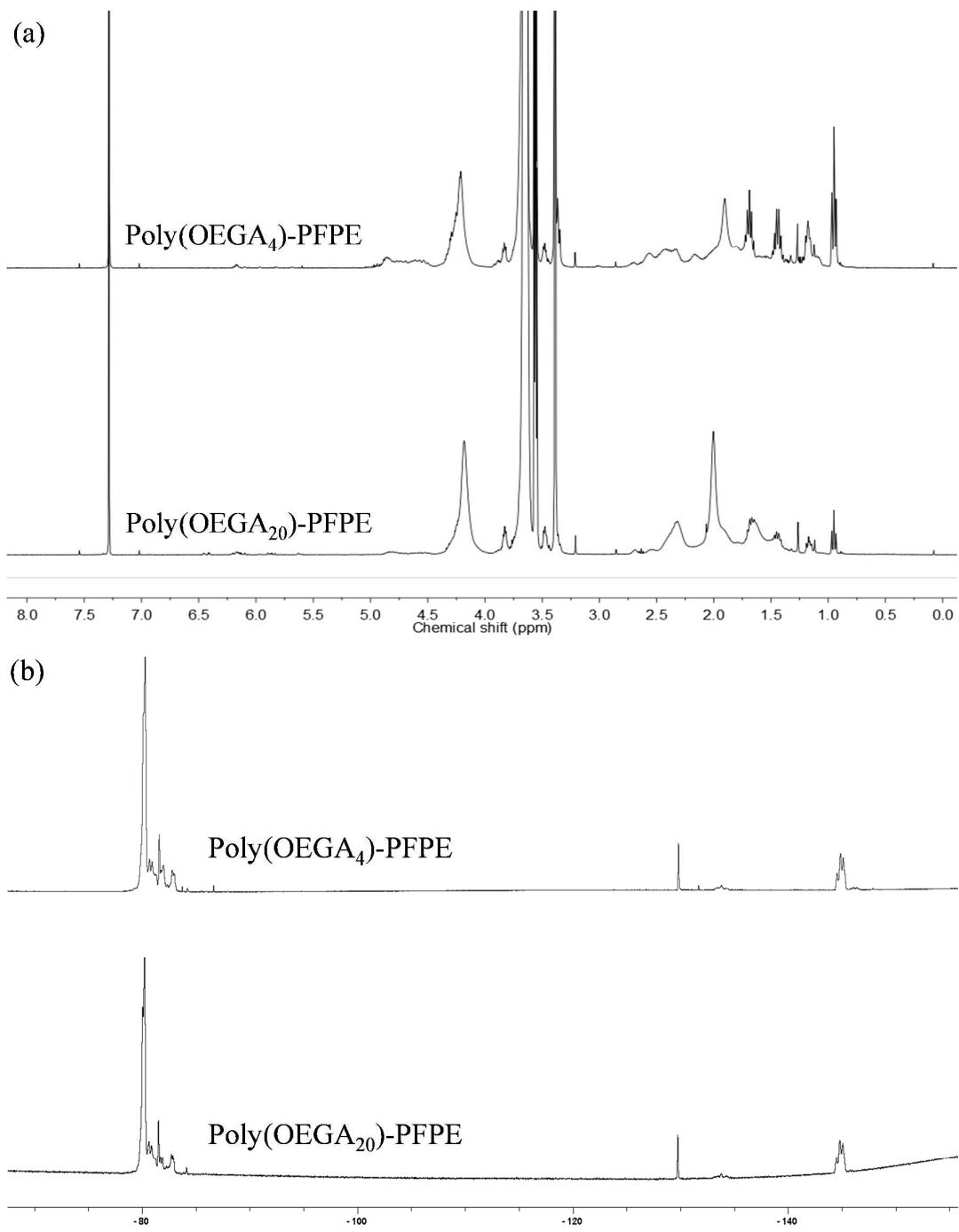
**Figure S3.**  $^1\text{H}$  NMR spectra of the crude poly(OEGA)<sub>m</sub>-PFPE polymers in  $\text{CDCl}_3$ . OEGA monomer conversion was 88.0, 89.4 and 97.2 % for poly(OEGA)<sub>4</sub>-PFPE, poly(OEGA)<sub>10</sub>-PFPE and poly(OEGA)<sub>20</sub>-PFPE, respectively.



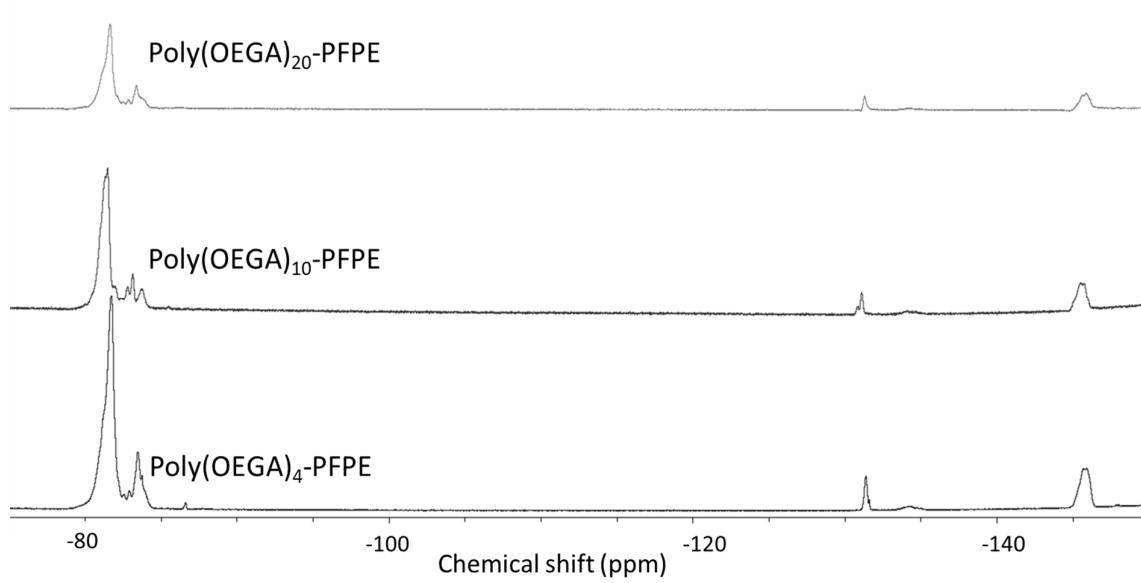
**Figure S4.** SEC chromatograms of the PFPE-based polymers obtained by RAFT polymerization. THF was used as the eluent.



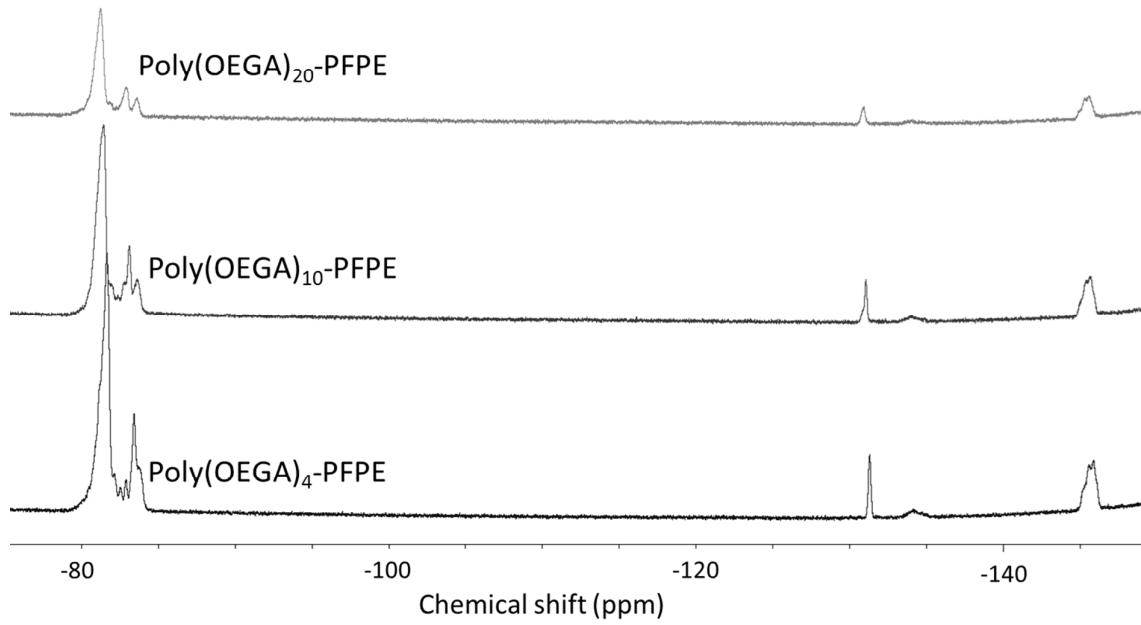
**Figure S5.** (a) and (b) The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra in  $\text{CDCl}_3$  and assignments to the spectra of poly(OEGA<sub>10</sub>)-PFPE. (c) The chemical structure of the poly(OEGA<sub>10</sub>)-PFPE synthesized through RAFT polymerisation.



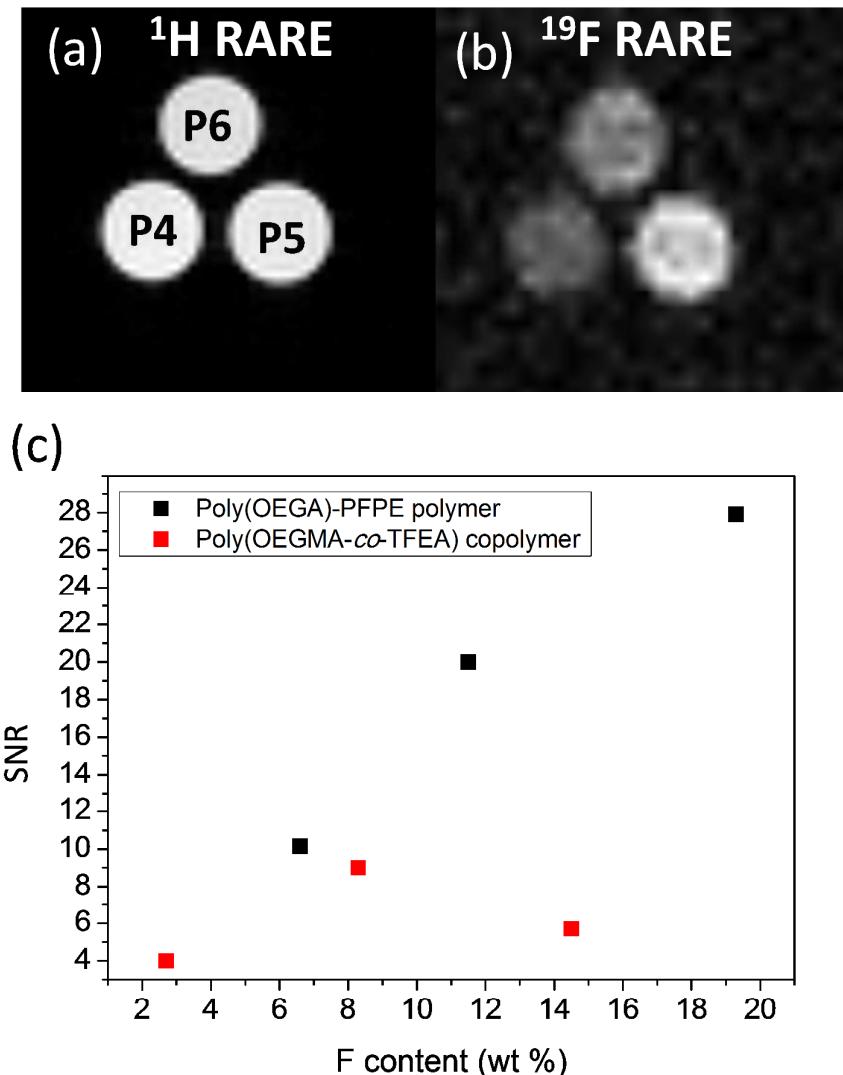
**Figure S6.** The (a) <sup>1</sup>H and (b) <sup>19</sup>F NMR spectra of the poly(OEGA)<sub>4</sub>-PFPE and poly(OEGA)<sub>20</sub>-PFPE polymers in CDCl<sub>3</sub>.



**Figure S7.**  $^{19}\text{F}$  NMR spectra of the PFPE-based polymers in PBS/D<sub>2</sub>O (V/V 90/10) at a concentration of 20 mg/mL.



**Figure S8.**  $^{19}\text{F}$  NMR spectra of the PFPE-terminated polymers in the presence of serum (10 %).



**Figure S9.** *In vitro* MR spin-echo images of the poly(OEGMA-*co*-TFEA) polymers in PBS at 20 mg/mL: (a) and (b)  $^1\text{H}$  and  $^{19}\text{F}$  RARE images. (c) The signal-to-noise ratio (SNR) obtained from the  $^{19}\text{F}$  MR images of the PFPE-based (filled black symbols) and poly(OEGMA-*co*-TFEA) polymers (filled red symbols) with different fluorine contents.

**Table S1.** The detailed structural characteristics of the poly(OEGMA-*co*-TFEA) polymers.

Data are expressed as mean  $\pm$  SD (n=3).

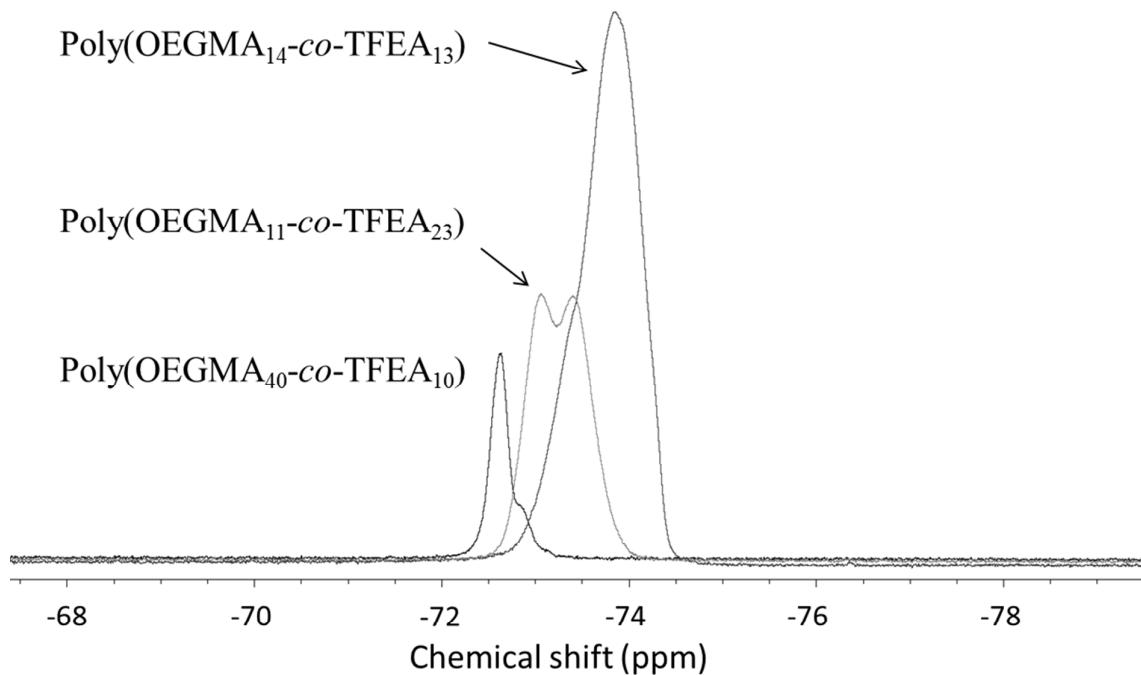
		Conversion OEGMA TFEA (%)	Fluorine content <sup>a</sup> (wt %)	$M_{n,\text{SEC}}^b$ (g/mol)	$M_{n,\text{NMR}}^c$ (g/mol)	$D_M^b$	$D_h^d$ (nm)
P4	Poly(OEGMA <sub>40</sub> - <i>co</i> -TFEA <sub>10</sub> )	92.6 83.3	2.7	11870	20800	1.13	4.8 $\pm$ 0.2
P5	Poly(OEGMA <sub>14</sub> - <i>co</i> -TFEA <sub>13</sub> )	78.3 52.2	8.3	7380	8900	1.17	9.6 $\pm$ 0.3
P6	Poly(OEGMA <sub>11</sub> - <i>co</i> -TFEA <sub>23</sub> )	84.5 58.4	14.5	5400	9000	1.15	36.5 $\pm$ 0.4

<sup>a</sup>the weight percentage of fluorine in the samples. <sup>b</sup> $M_{n,\text{SEC}}$  and  $D_M$  were acquired by SEC RI detector. <sup>c</sup>The calculations for the poly(OEGMA-*co*-TFEA) were reported in our previous publications.<sup>9</sup> <sup>d</sup> $D_h$  was obtained by DLS in water and based on the number-average values.

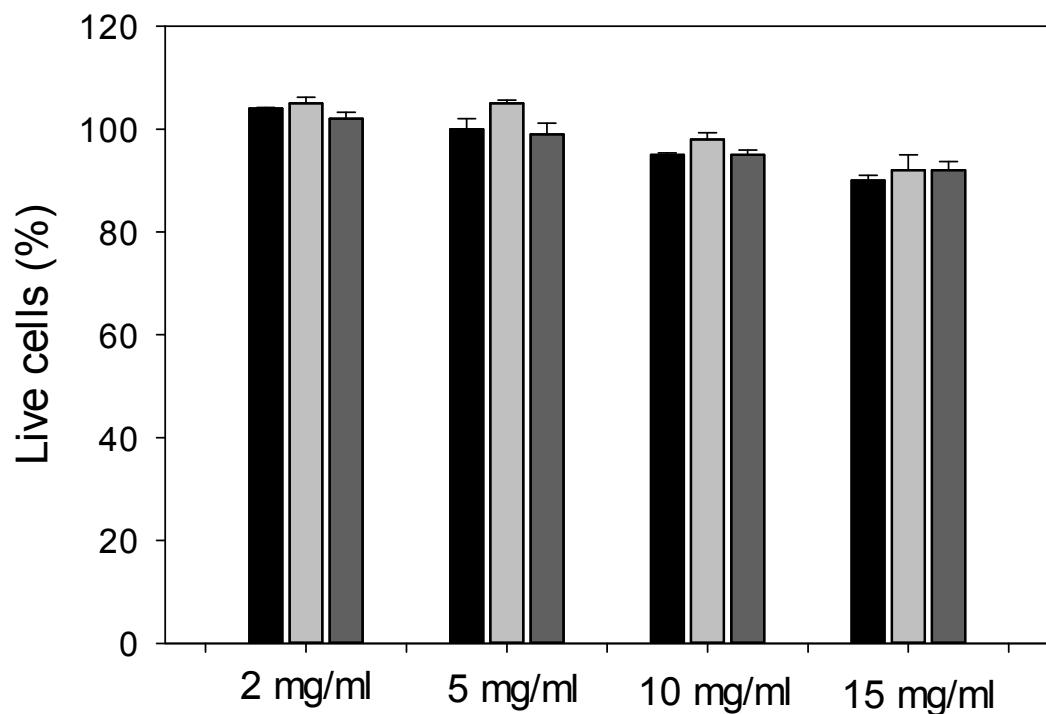
**Table S2.** NMR and MRI properties of poly(OEGMA-*co*-TFEA) in PBS. Data are expressed as mean  $\pm$  SD (n=3).

Samples	Fluorine content (wt%)	$^{19}\text{F}$ NMR T <sub>1</sub> /T <sub>2</sub> (ms) <sup>a</sup>	$^{19}\text{F}$ concentration (M) <sup>b</sup>	Image SNR <sup>c</sup>
Poly(OEGMA <sub>40</sub> - <i>co</i> -TFEA <sub>10</sub> )	2.7	484.2/152.1	0.028	4.0 $\pm$ 0.25
Poly(OEGMA <sub>14</sub> - <i>co</i> -TFEA <sub>13</sub> )	8.3	440.5/80.8	0.087	9.0 $\pm$ 0.29
Poly(OEGMA <sub>11</sub> - <i>co</i> -TFEA <sub>23</sub> )	14.5	441.3/46.8	0.15	5.7 $\pm$ 0.32

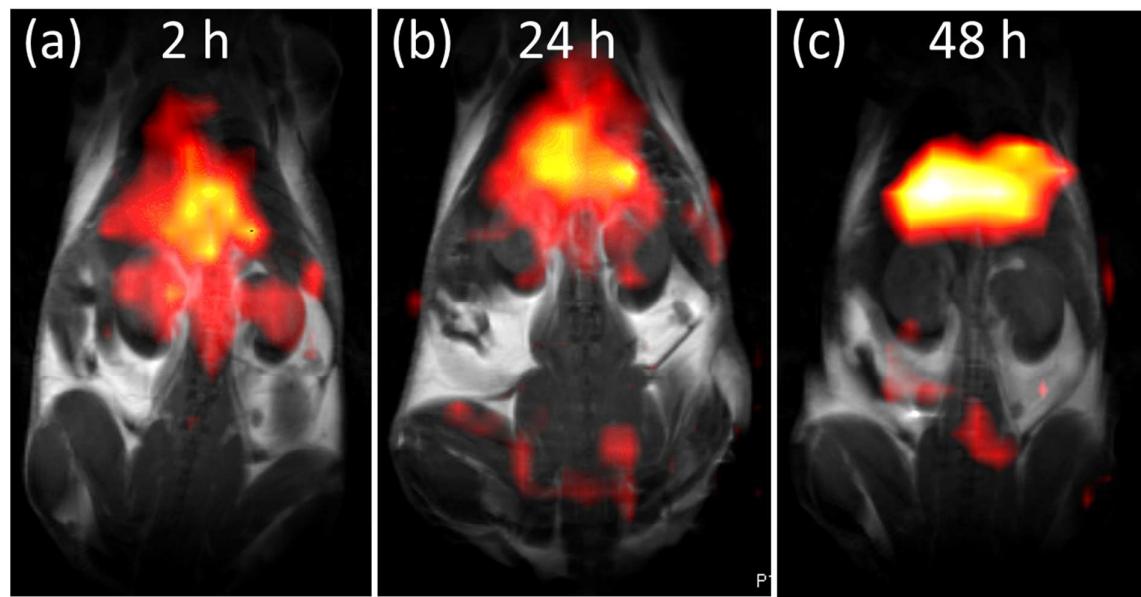
<sup>a</sup>The  $^{19}\text{F}$  NMR T<sub>1</sub>/T<sub>2</sub> were tested in PBS/D<sub>2</sub>O (90/10, v/v) at 310 K. <sup>b</sup> The  $^{19}\text{F}$  concentration of the polymers in PBS solutions. <sup>c</sup> The image SNR was calculated from the  $^{19}\text{F}$  MRI images.



**Figure S10.**  $^{19}\text{F}$  NMR spectra of the poly(OEGMA-*co*-TFEA) copolymers.



**Figure S11.** Viability of MCF-7 cancer cells after incubation with P1, P2 and P3 polymers at different concentrations for 24 h. The results are the average of three replicates  $\pm$  standard deviation.



**Figure S12.** *In vivo*  $^1\text{H}/^{19}\text{F}$  MRI of the poly(OEGA)<sub>4</sub>-PFPE in mouse on a 9.4 T MRI scanner.  
(a) 2h, (b) 24 h and (c) 48 h after intravenous injection.

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