

# PEGylated amphiphilic polymeric manganese(II) complex as magnetic resonance angiographic agent

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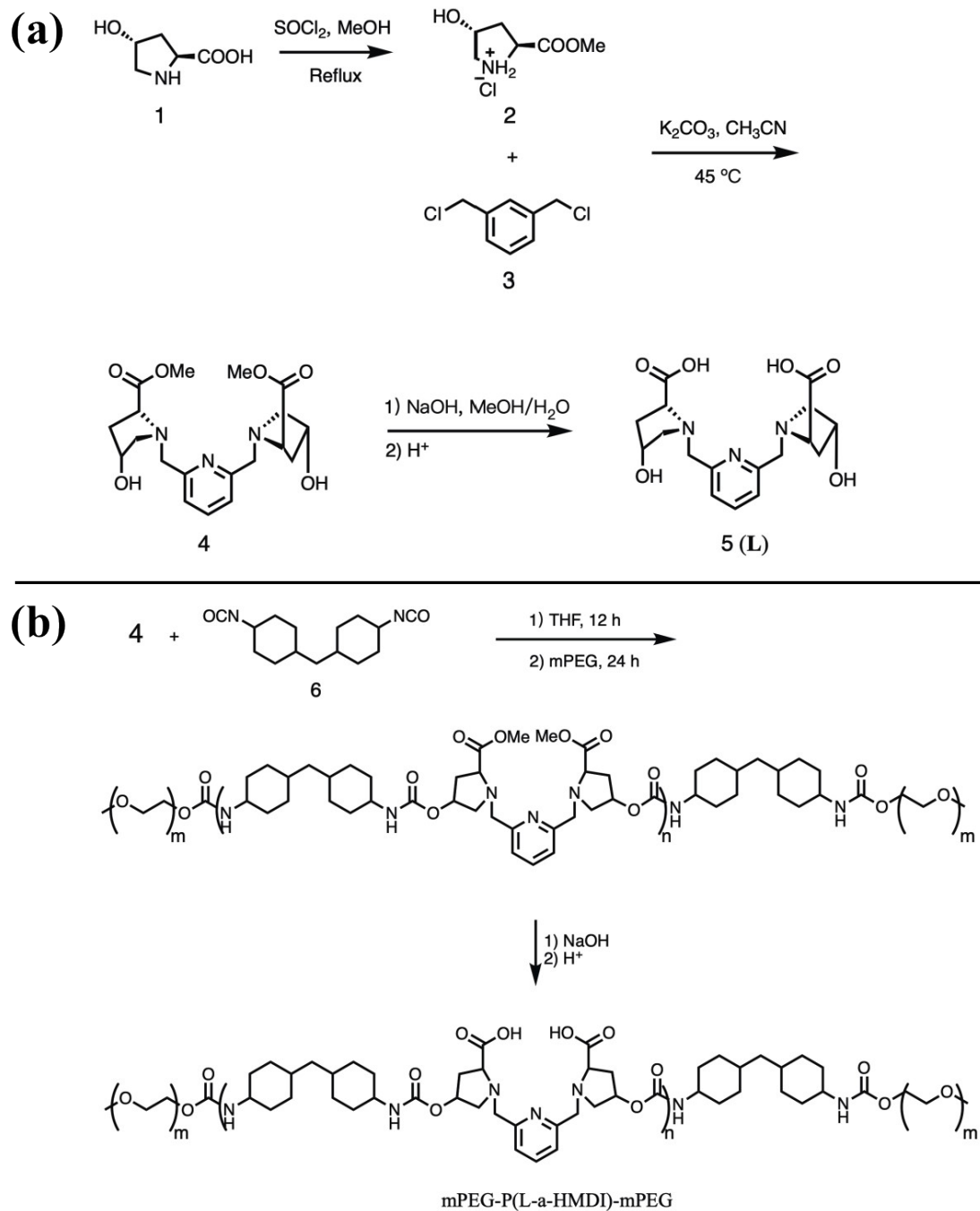
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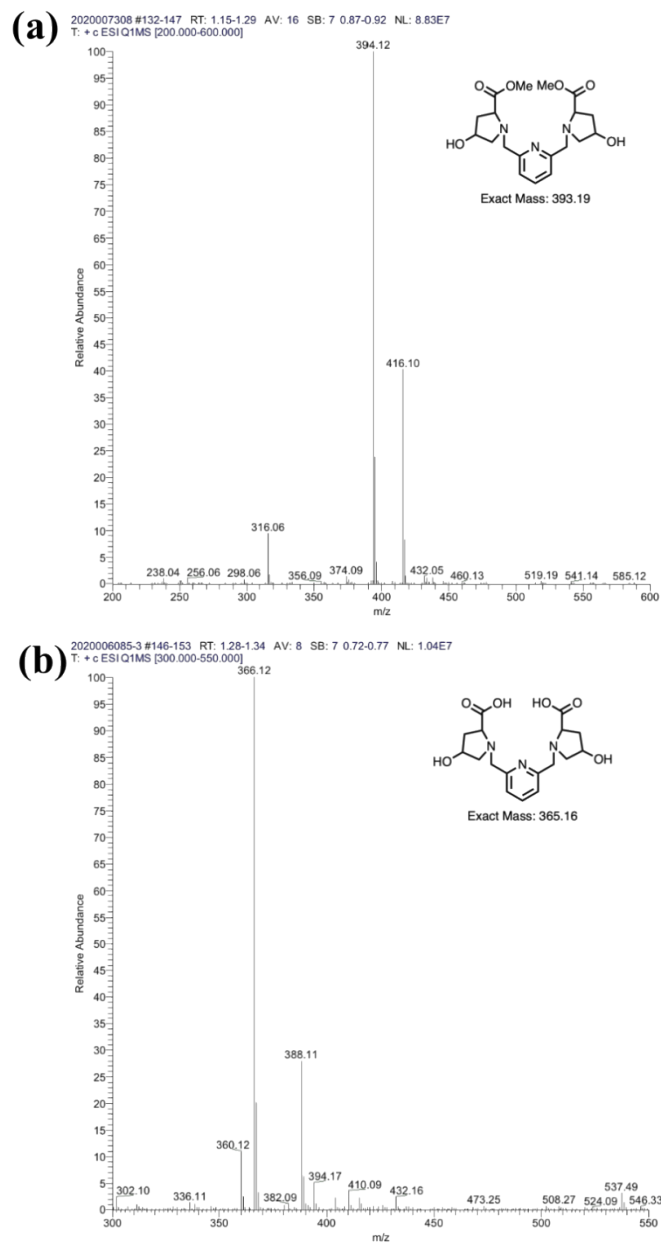
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**Scheme S1.** Synthesis of the small molecule ligand **L** (a) and mPEG-P(L-a-HMDI)-mPEG (b).



**Figure S1.** Electrospray ionization mass spectrometry (ESI-MS) spectrum of compound 4 (a) and L (b).

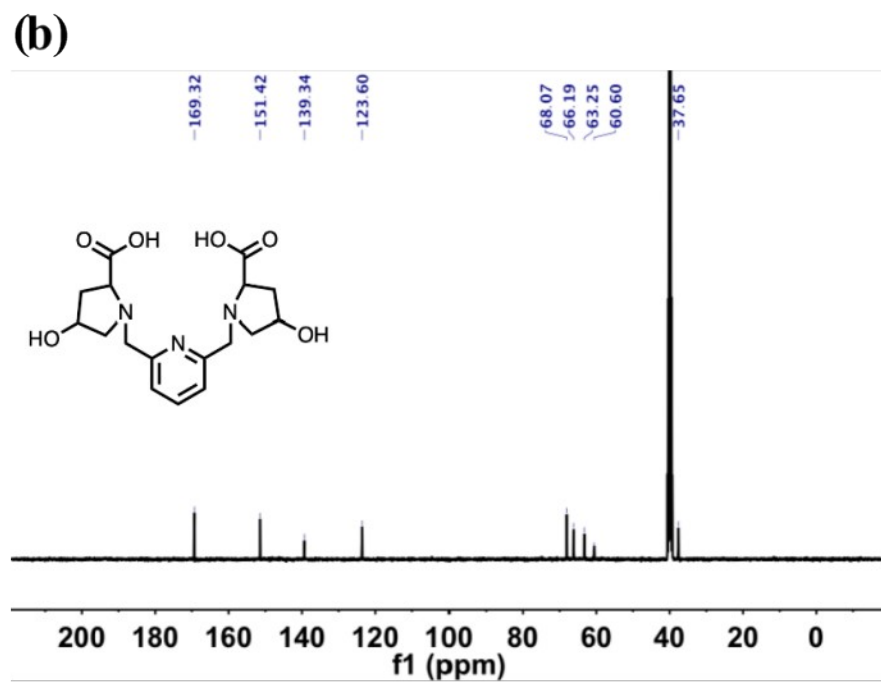
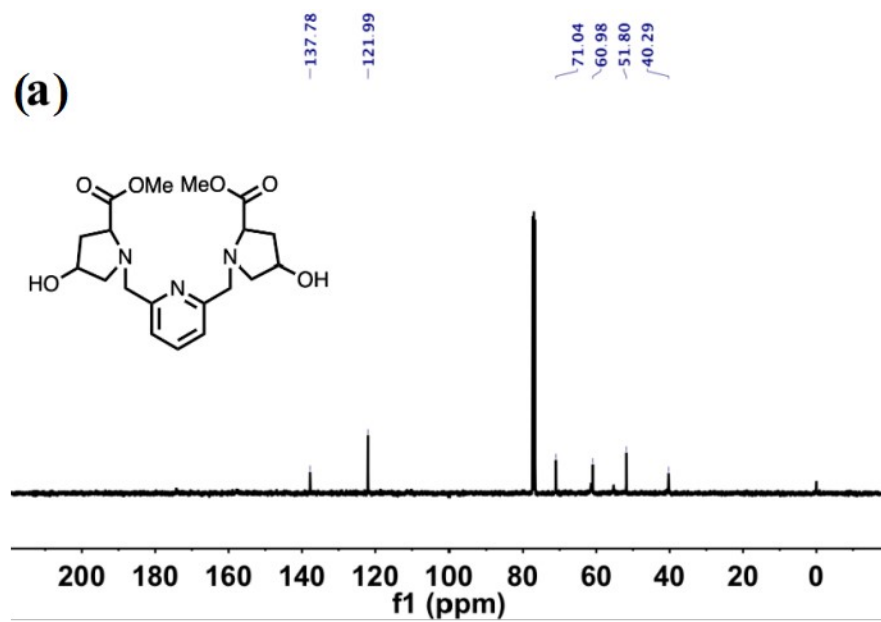
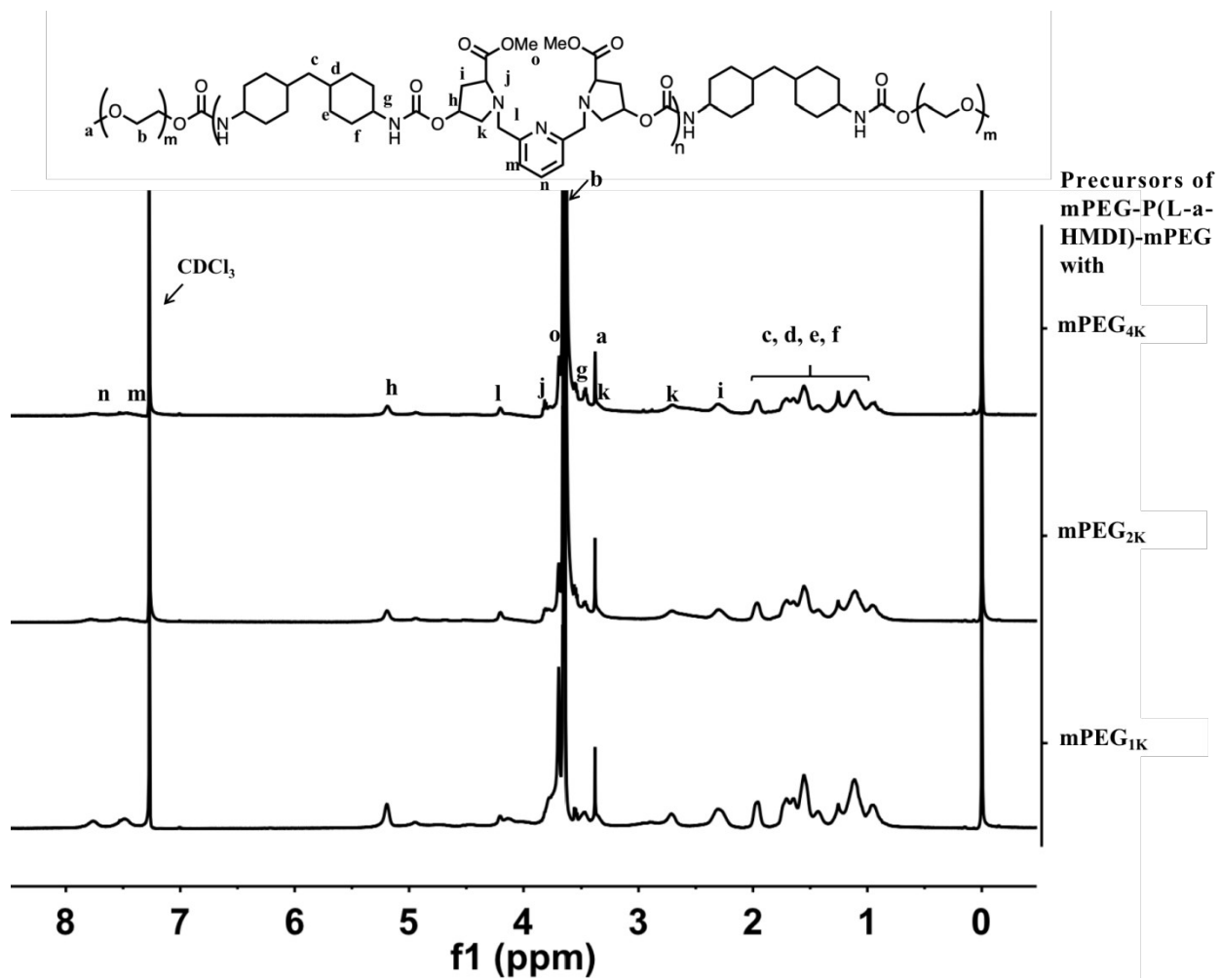
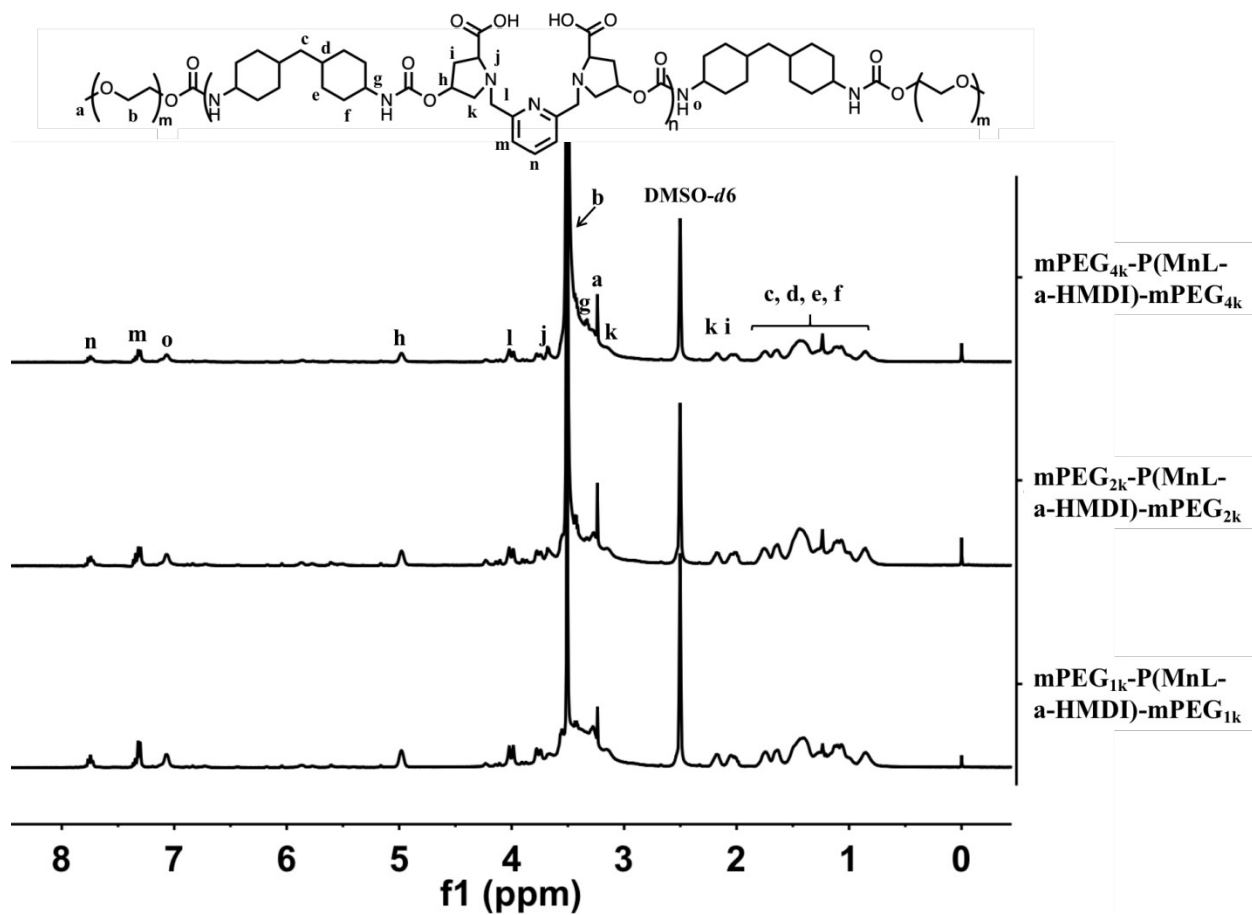


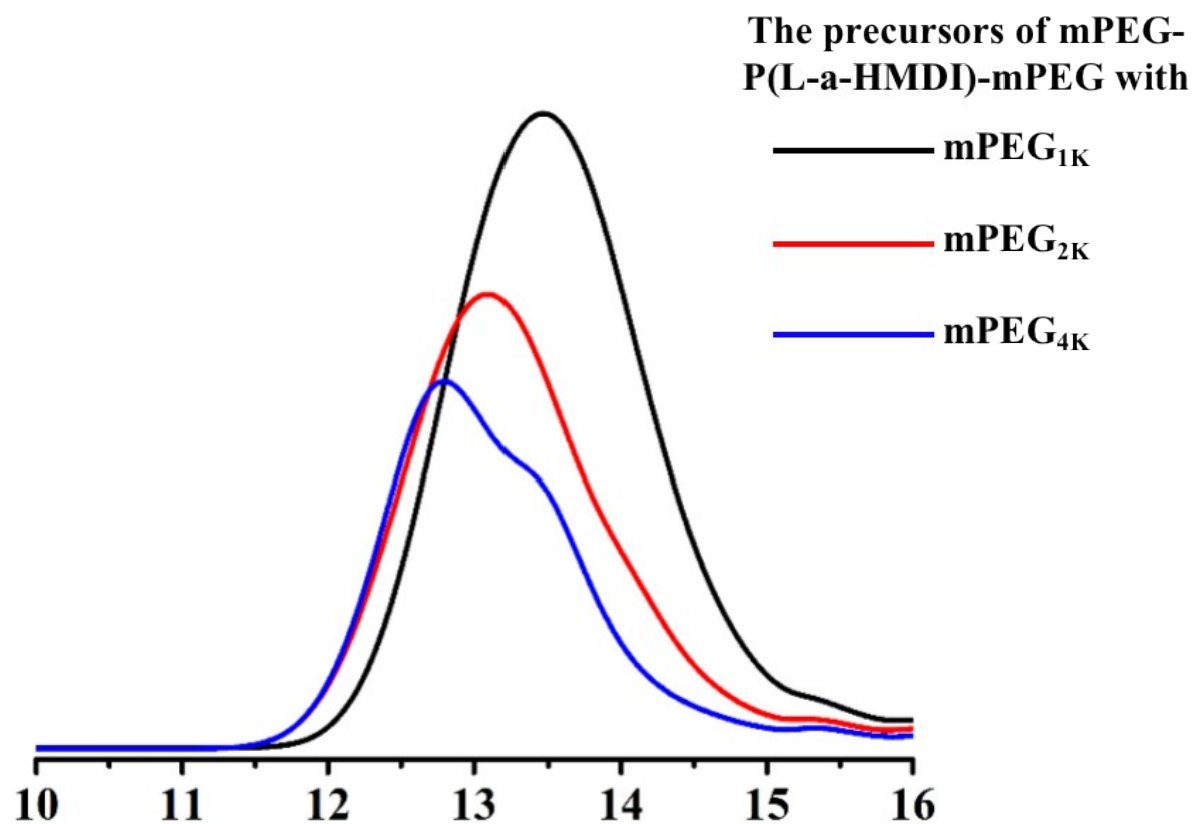
Figure S2.  $^{13}\text{C}$  NMR spectrum of compound 4 (a) and L (b).



**Figure S3.** <sup>1</sup>H NMR spectrum of the precursors of mPEG-P(L-a-HMDI)-mPEG with different molecular weight of mPEG (1 kD, 2 kD and 4 kD).



**Figure S4.**  $^1\text{H}$  NMR spectrum of mPEG-P(L-a-HMDI)-mPEG with different molecular weight of mPEG (1 kD, 2 kD and 4 kD).

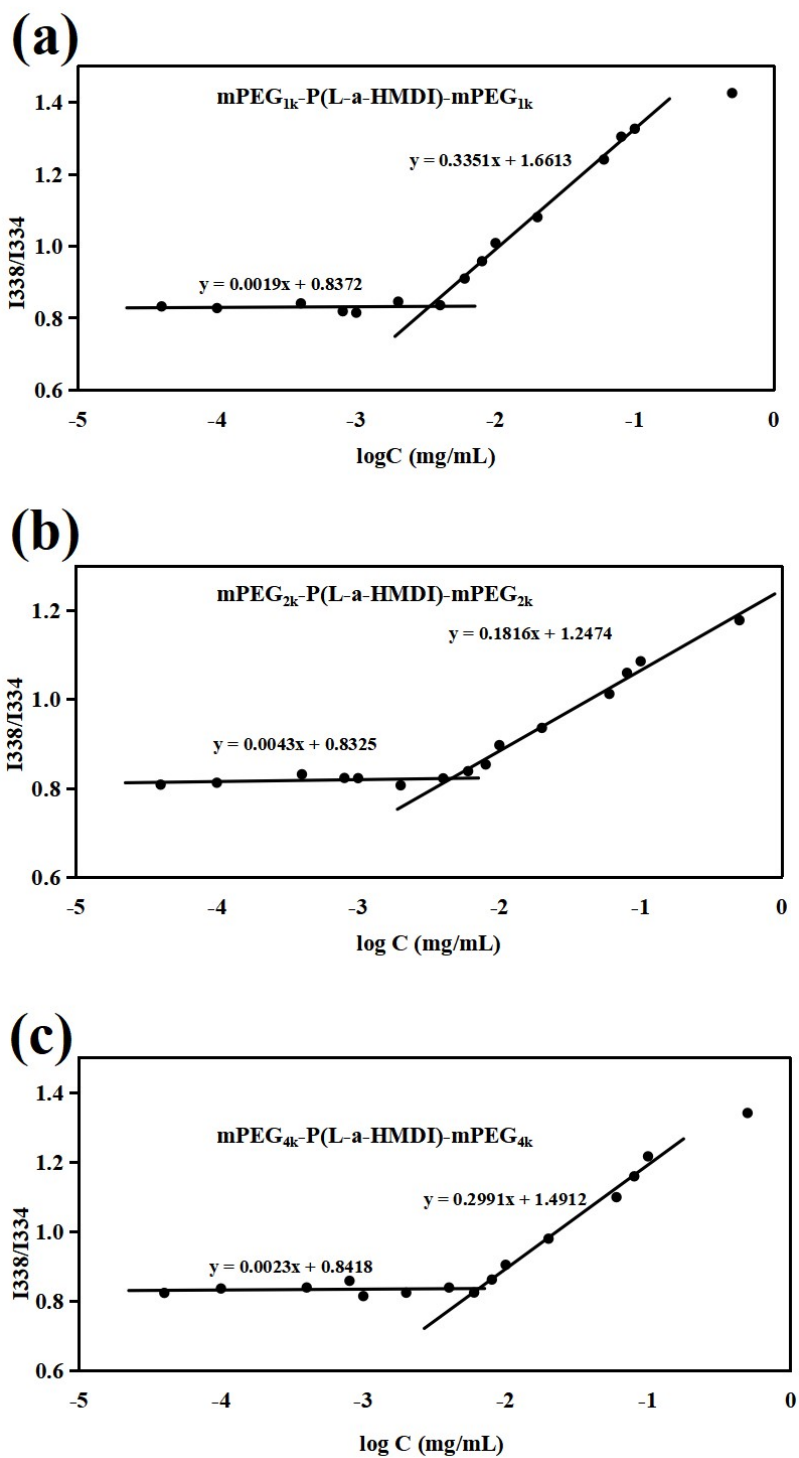


**Figure S5.** Gel permeation chromatography (GPC) of the precursors of mPEG-P(L-a-HMDI)-mPEG with different molecular weight of mPEG (1 kD, 2 kD and 4 kD ).

**Table S1.** The molecular weight of the precursors of mPEG-P(L-a-HMDI)-mPEG with different molecular weight of mPEG (1 kD, 2 kD or 4 kD).

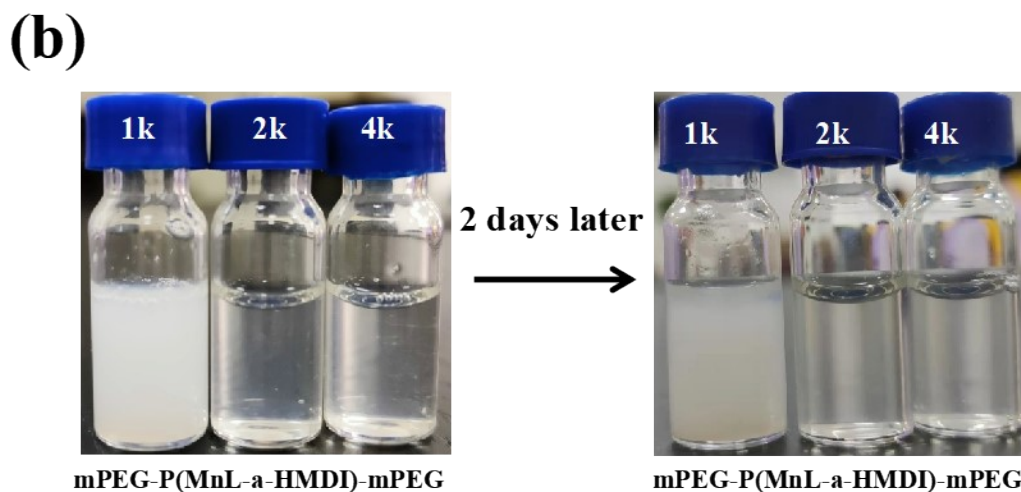
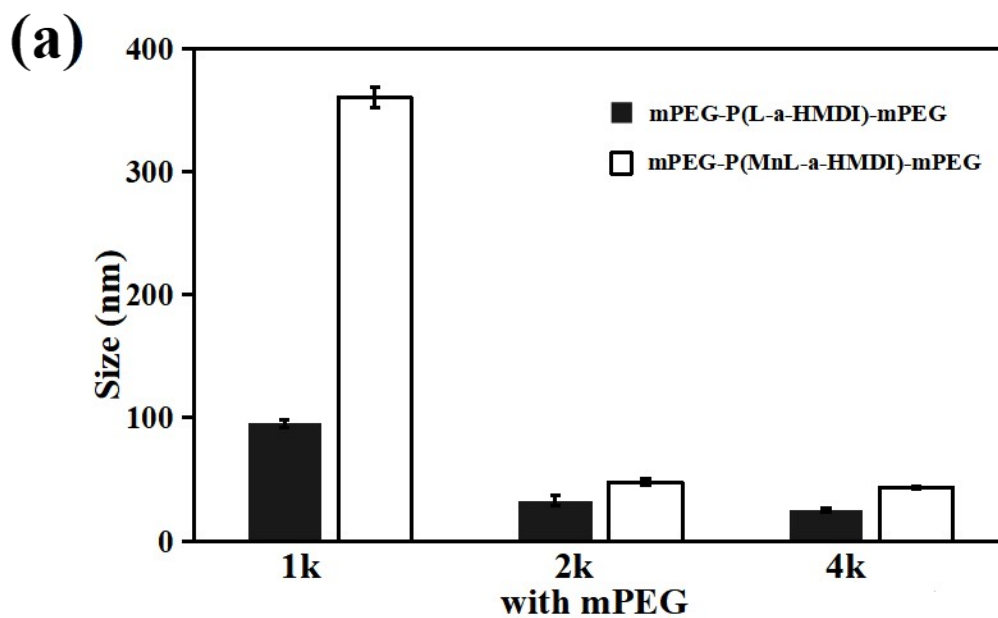
Sample	Yield(%)	Mn <sup>a</sup> (kg/mol)	Mn <sup>b</sup> (kg/mol)	Mw <sup>b</sup> (kg/mol)	PDI <sup>b</sup>
mPEG <sub>1k</sub>	72	6.7	5.9	9.4	1.59
mPEG <sub>2k</sub>	78	8.0	8.1	12.7	1.57
mPEG <sub>4k</sub>	81	10.8	10.7	15.9	1.48

<sup>a</sup>Determined by <sup>1</sup>H NMR; <sup>b</sup>Determined by GPC (eluent: DMF, flow rate: 0.4 mL/min).

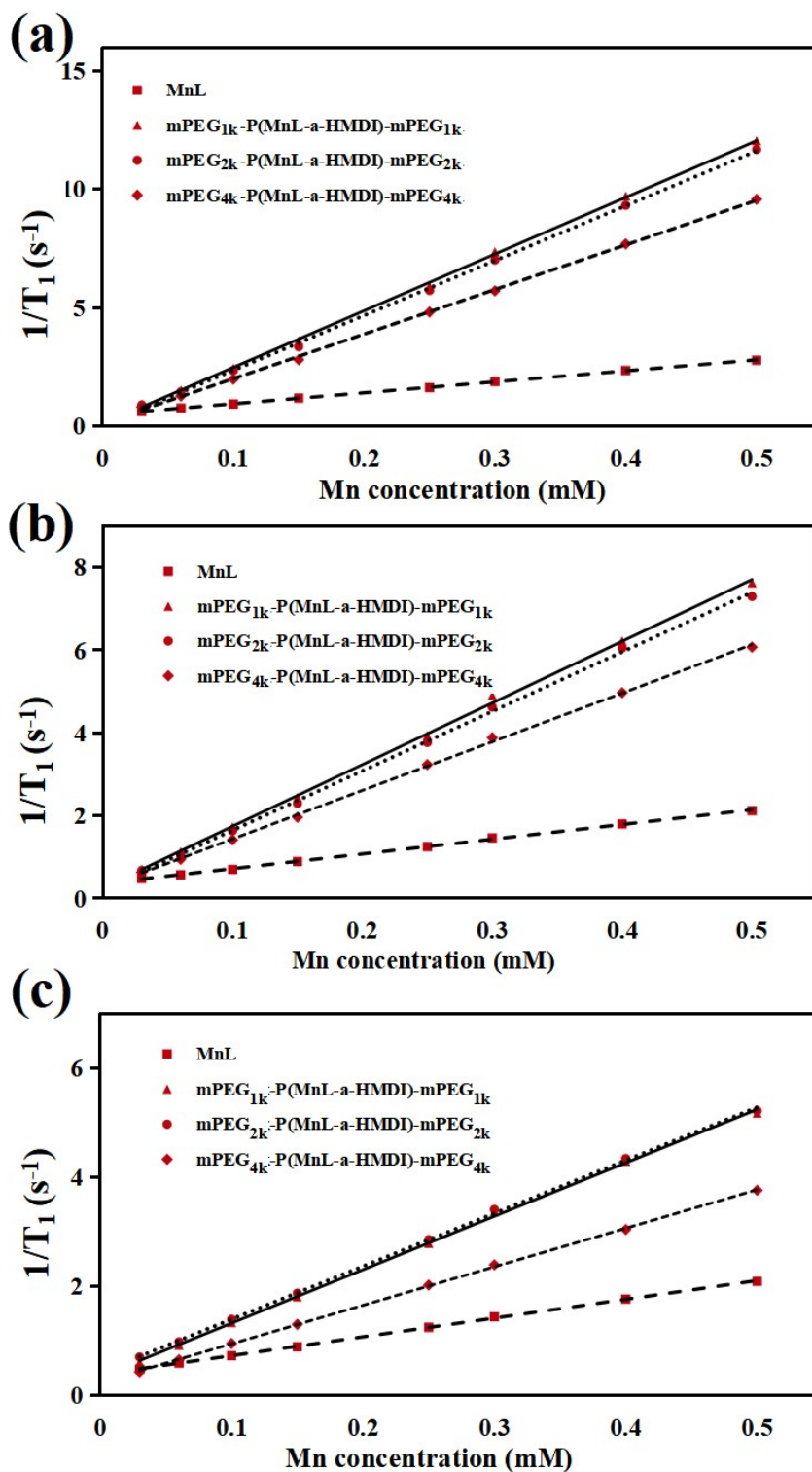


**Figure S6.** CMC of mPEG-P(L-a-HMDI)-mPEG with different molecular weight of mPEG (1 kD, 2 kD and 4 kD).

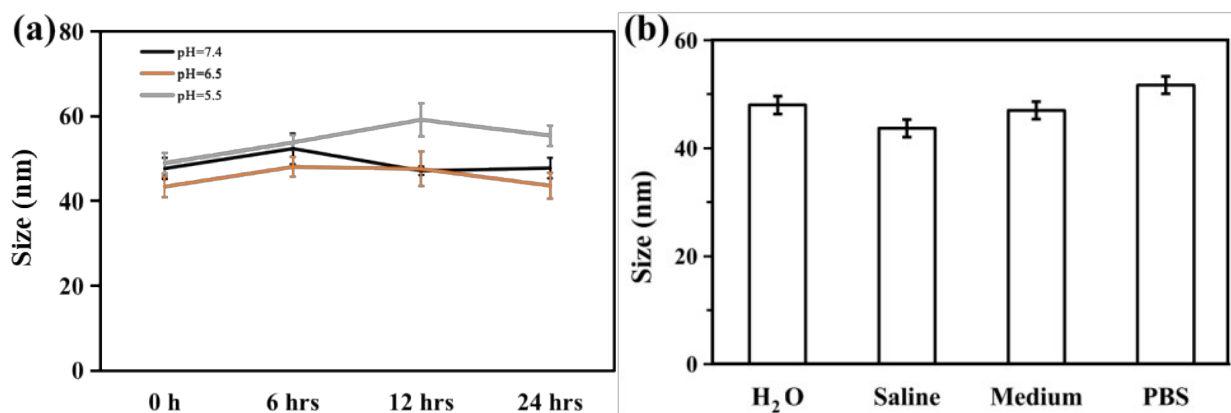




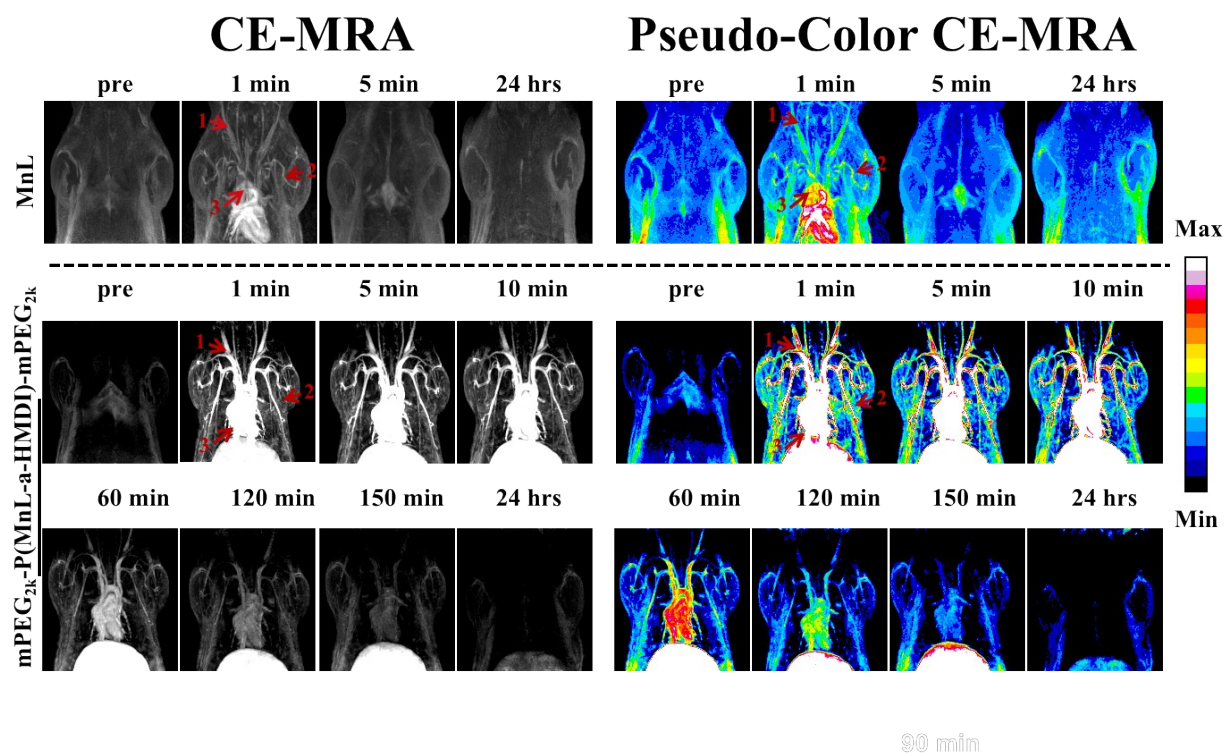
**Figure S7.** (a) Particle size of three mPEG-P(L-a-HMDI)-mPEG polymer micelles and their Mn complexes. (b) After 2 days standing, visible sediments appeared in the bottle with mPEG<sub>1k</sub>-P(MnL-a-HMDI)-mPEG<sub>1k</sub>.



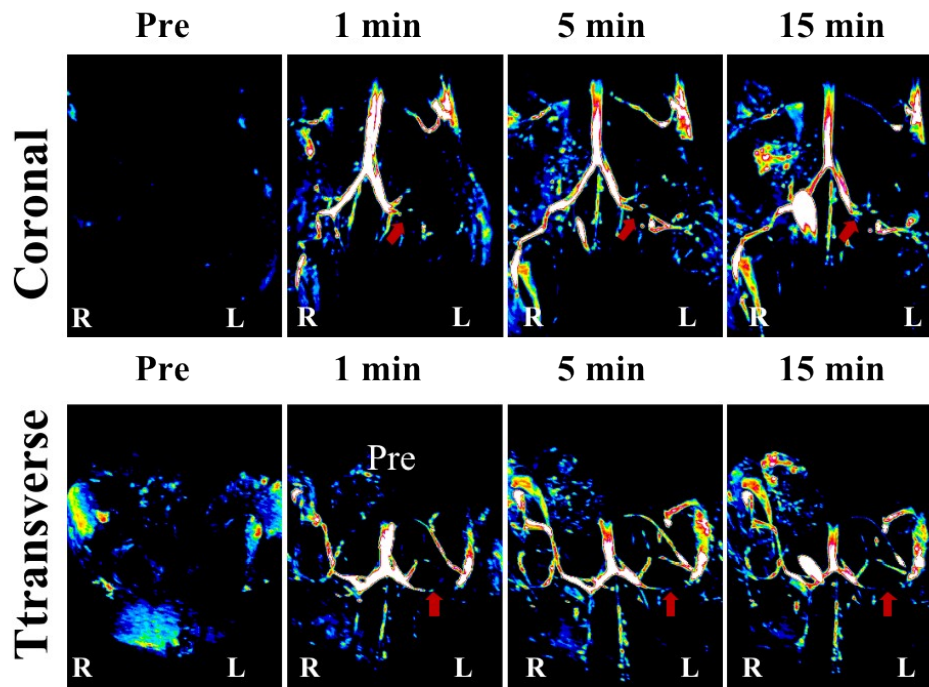
**Figure S8.**  $T_1$  relaxivity over Mn concentration at the magnetic field of (a) 0.5 T, (b) 1.5 T, (c) 3.0 T.



**Figure S9.** The changes in sizes of mPEG<sub>2k</sub>-P(MnL-a-HMDI)-mPEG<sub>2k</sub> complexes in different pH values (a) and several dispersion media (b).



**Figure S10.** Contrast enhanced magnetic resonance angiography (MRA) of SD rats on a clinical 3.0 T MR scanner at low dosage of 0.1 Mn mmol/kg BW.



**Figure S11.** The corresponding pseudo-color MRA images of rats with vascular stenosis in the right lower limb before and after intravenous injection of  $m\text{PEG}_{2k}\text{-P}(\text{MnL-a-HMDI})\text{-mPEG}_{2k}$  with 0.1 mmol Mn/kg BW. Among them, the vascular stenosis areas (red arrow) of blood vessels are almost invisible, which are obviously in contrast with the normal blood vessel on the right side and can be clearly detected.