

**Constructing pH-responsive poly(trimethylene carbonate) (PTMC)-
based polymersomes functionalized with cell-penetrating guanidines**

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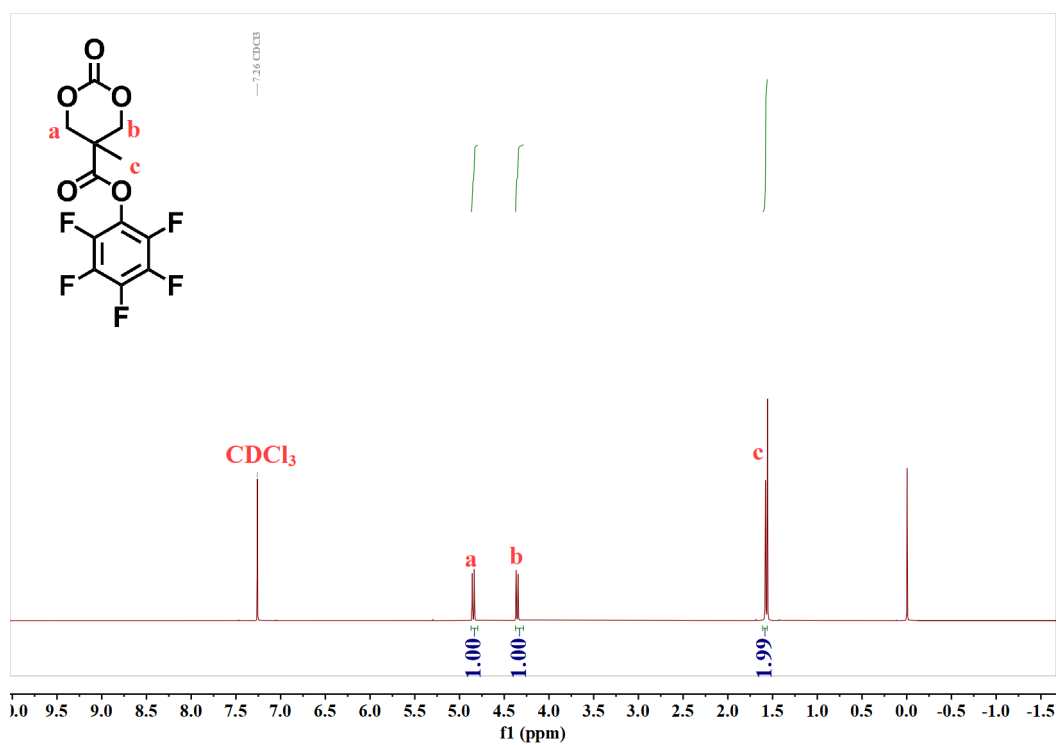


Fig. S1 ¹H NMR spectrum of TMC-OC₆F₅ in CDCl₃.

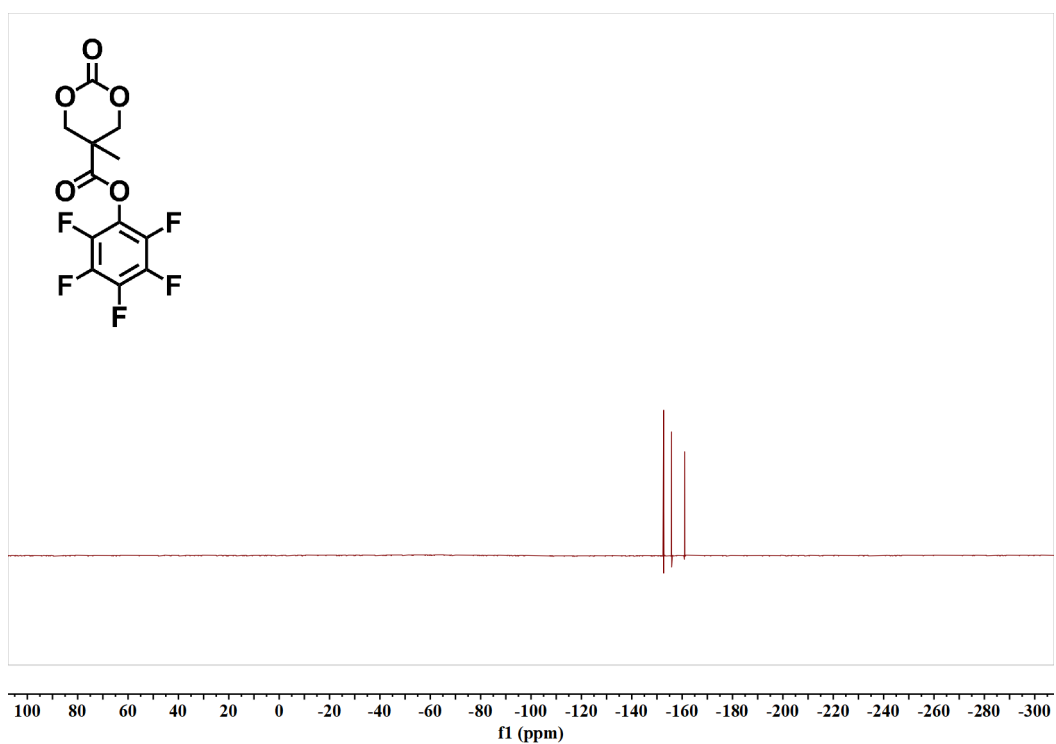


Fig. S2 ¹⁹F NMR spectrum of TMC-OC₆F₅ in CDCl₃.

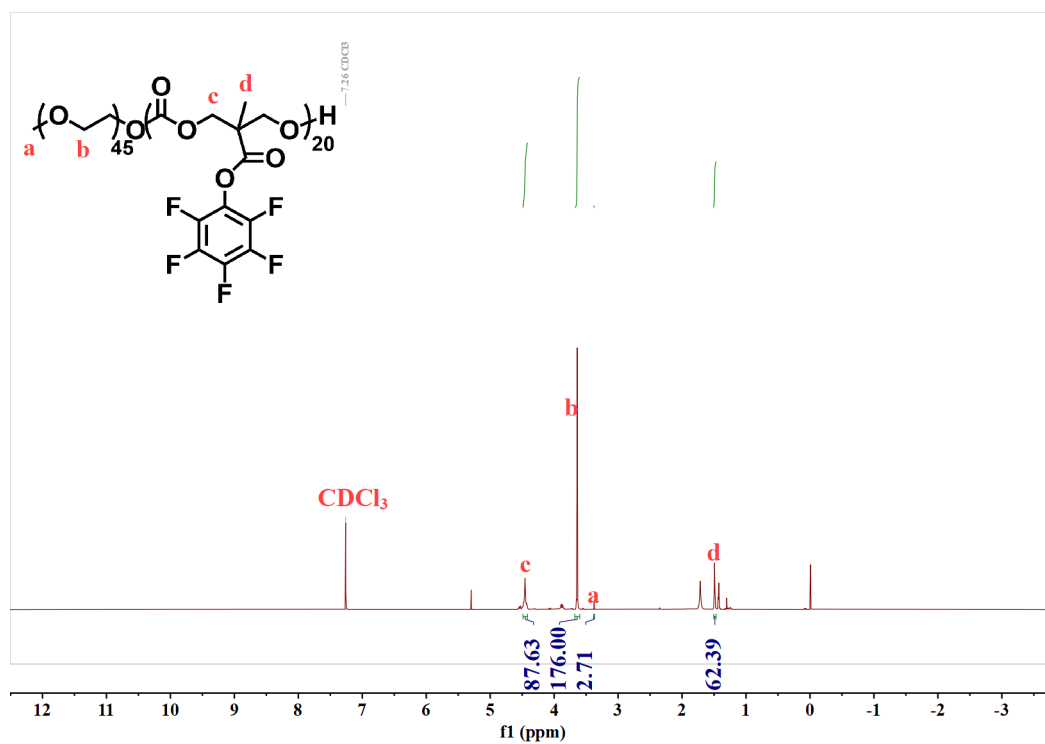


Fig. S3 ¹H NMR spectrum of PEG₄₅-b-P(TMC-OC₆F₅)₂₀ in CDCl₃.

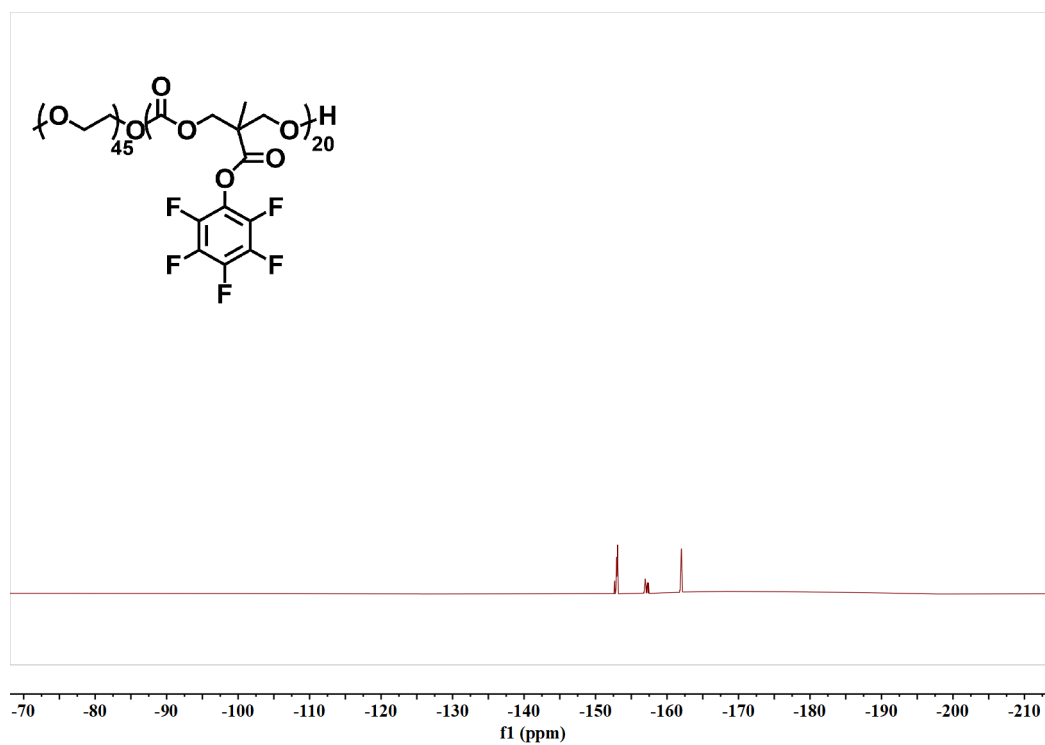


Fig. S4 ¹⁹F NMR spectrum of PEG₄₅-b-P(TMC-OC₆F₅)₂₀ in CDCl₃.

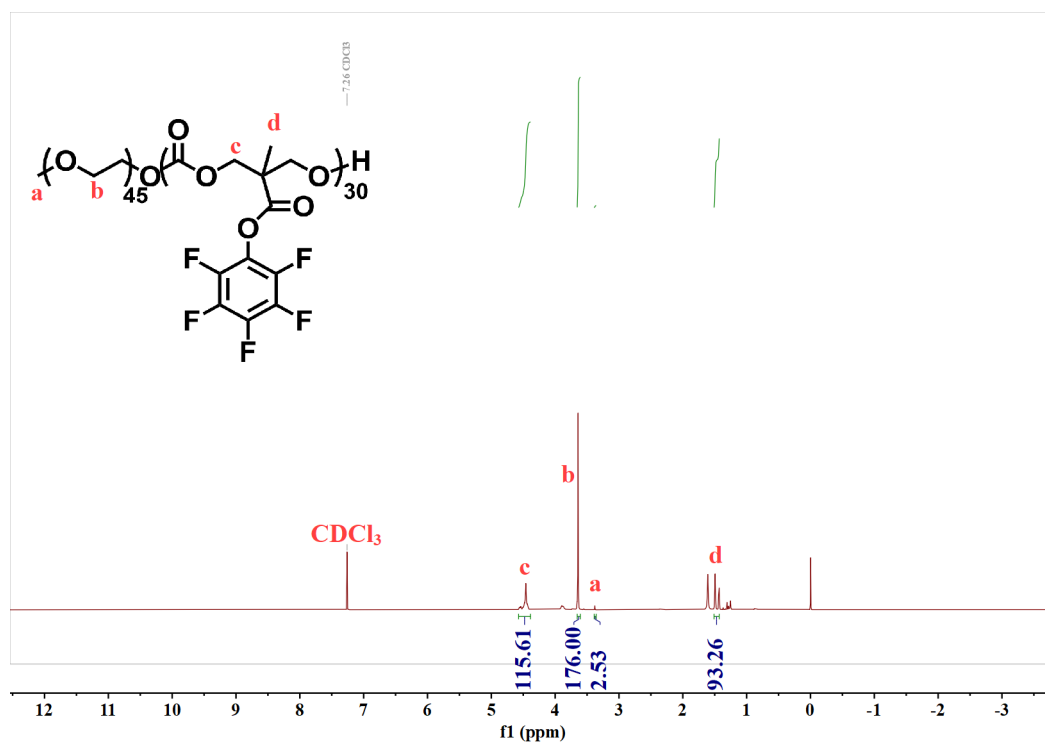


Fig. S5 ¹H NMR spectrum of PEG₄₅-b-P(TMC-OC₆F₅)₃₀ in CDCl₃.

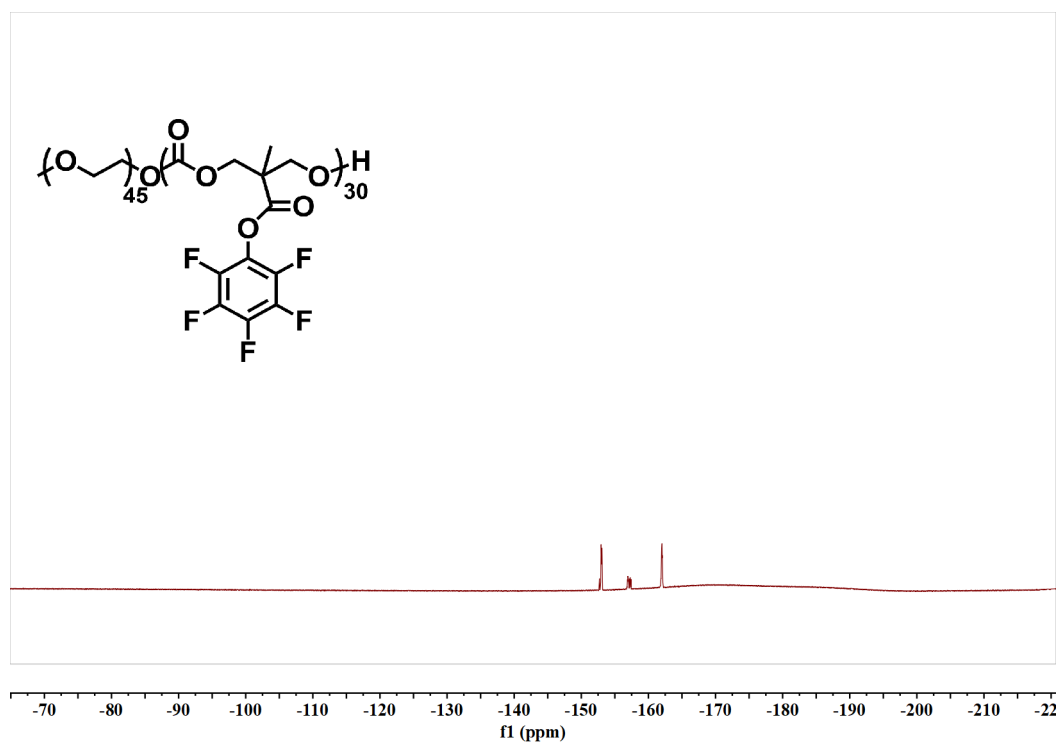


Fig. S6 ¹⁹F NMR spectrum of PEG₄₅-b-P(TMC-OC₆F₅)₃₀ in CDCl₃.

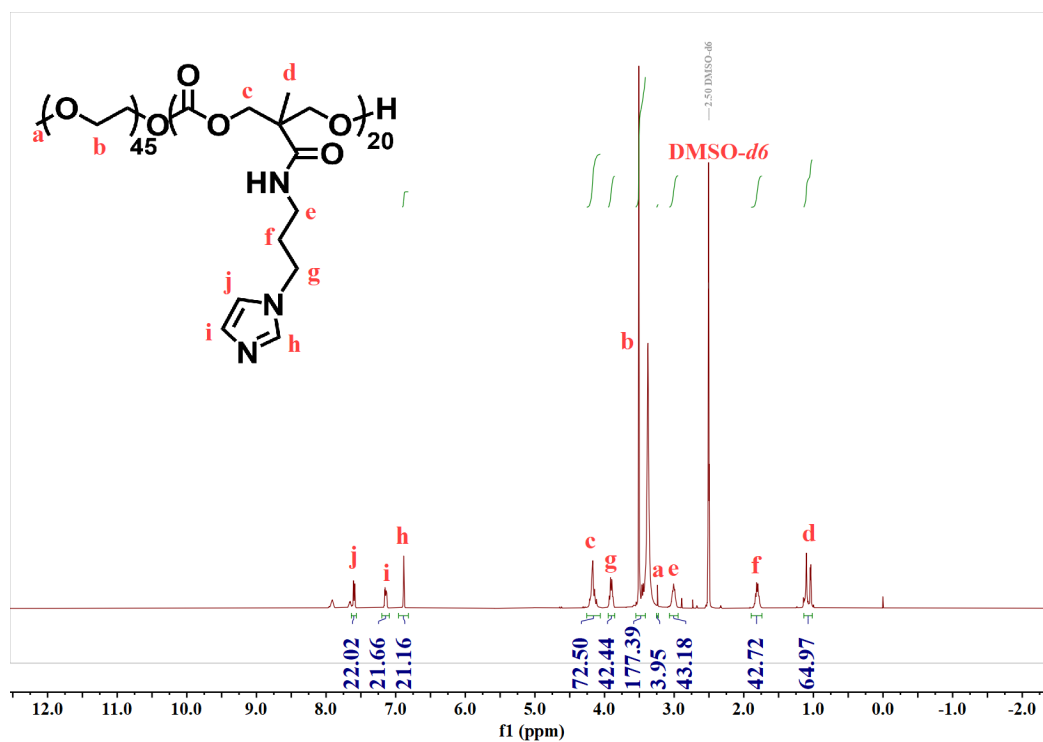


Fig. S7 ¹H NMR spectrum of PTMCIM-1 in DMSO-*d*₆.

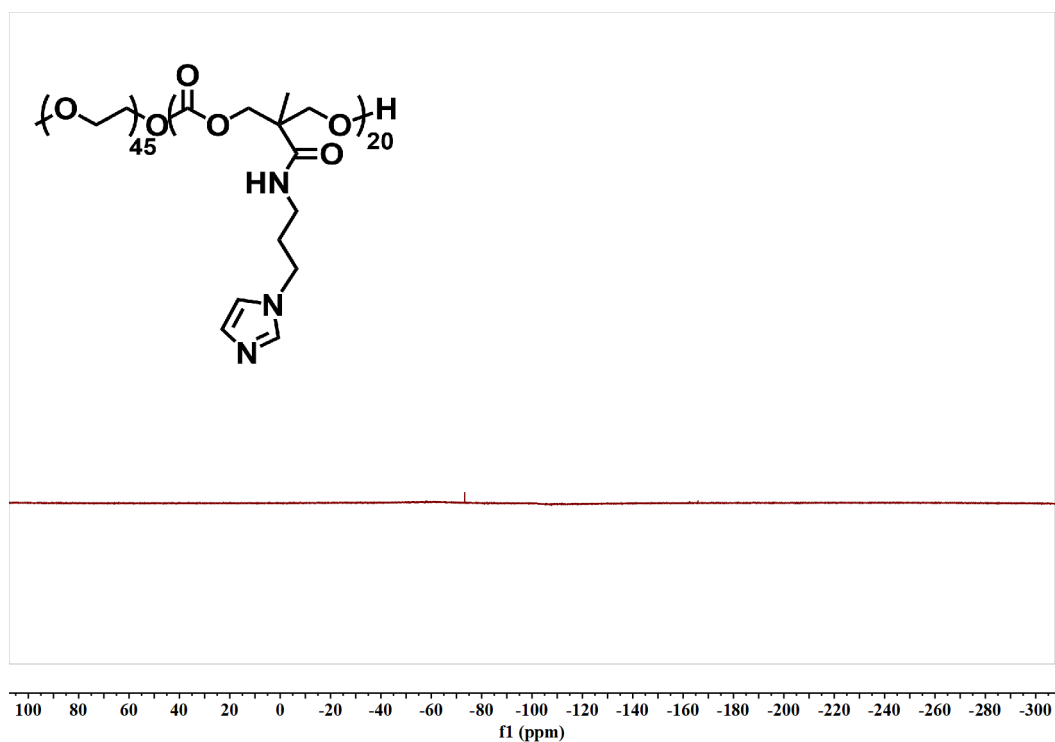


Fig. S8 ¹⁹F NMR spectrum of PTMCIM-1 in DMSO-*d*₆.

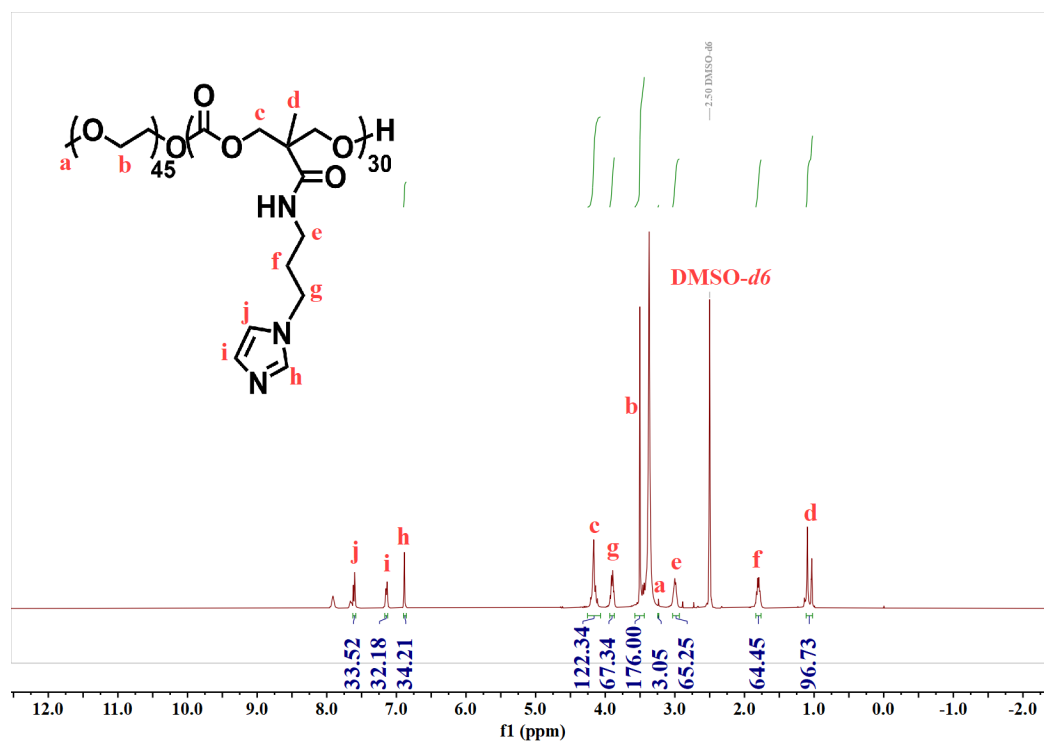


Fig. S9 ^1H NMR spectrum of PTMCIM-2 in $\text{DMSO-}d_6$.

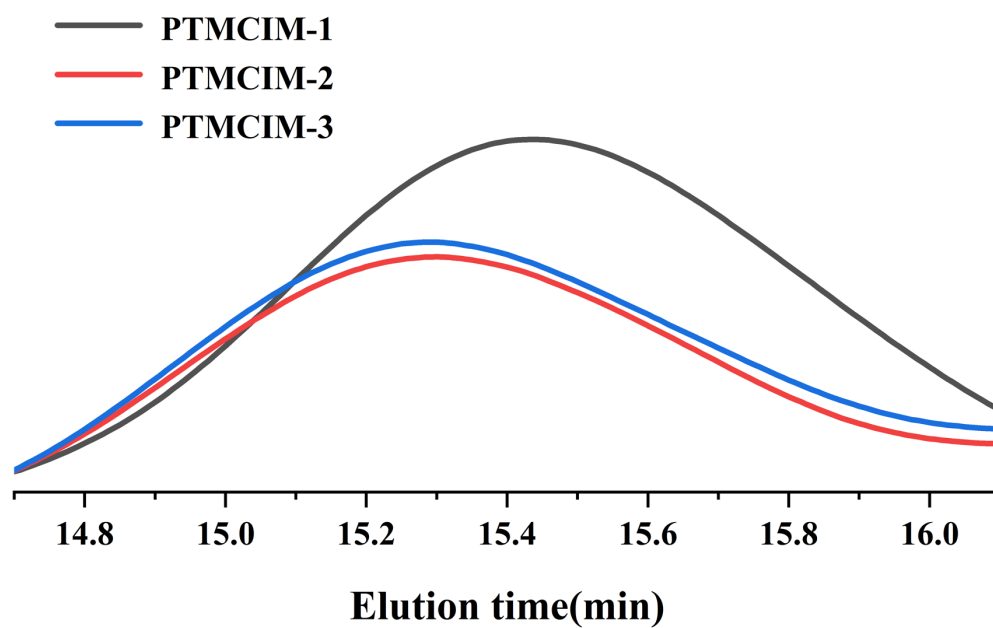


Fig. S10 SEC traces of $\text{PEG}_{45}\text{-}b\text{-P(TMCIM)}_n$ with different hydrophobic length.

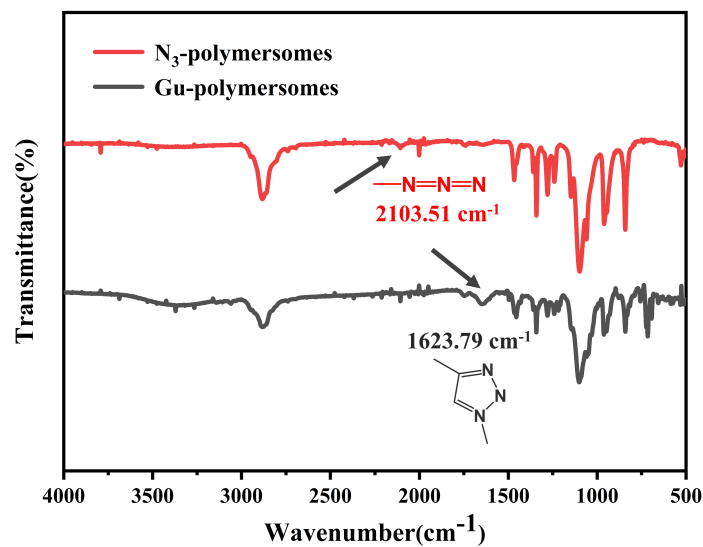


Fig. S11 The Fourier transform infrared (FTIR) characterization of N₃-polymersomes and Gu-polymersomes.

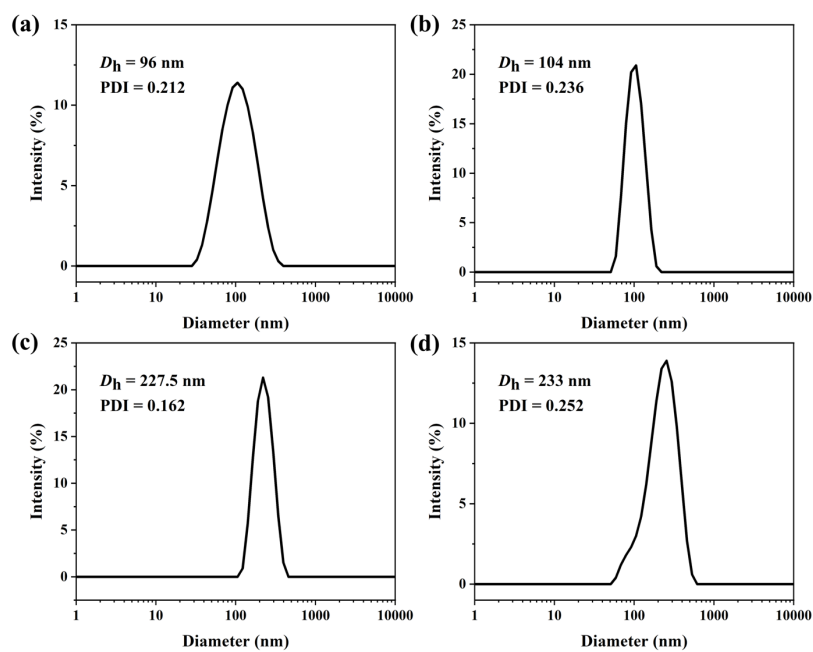


Fig. S12 DLS results of different polymer self-assemblies: (a) PTMCIM-1, (b) PTMCIM-2, (c) PTMCIM-3, and (d) Gu1-PTMCIM-3.

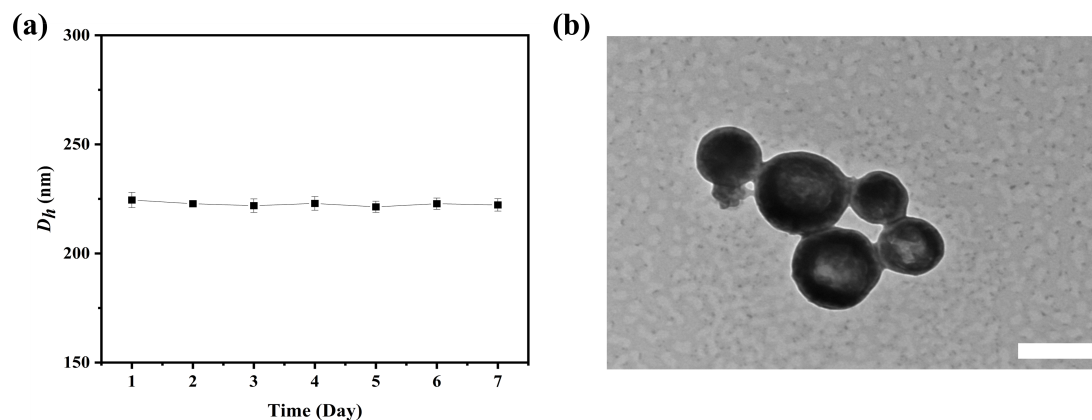


Fig. S13 (a) The size change of PTMCIM-3 at different times under physiological conditions and (b) the TEM image of PTMCIM-3 after 7 days under physiological conditions.

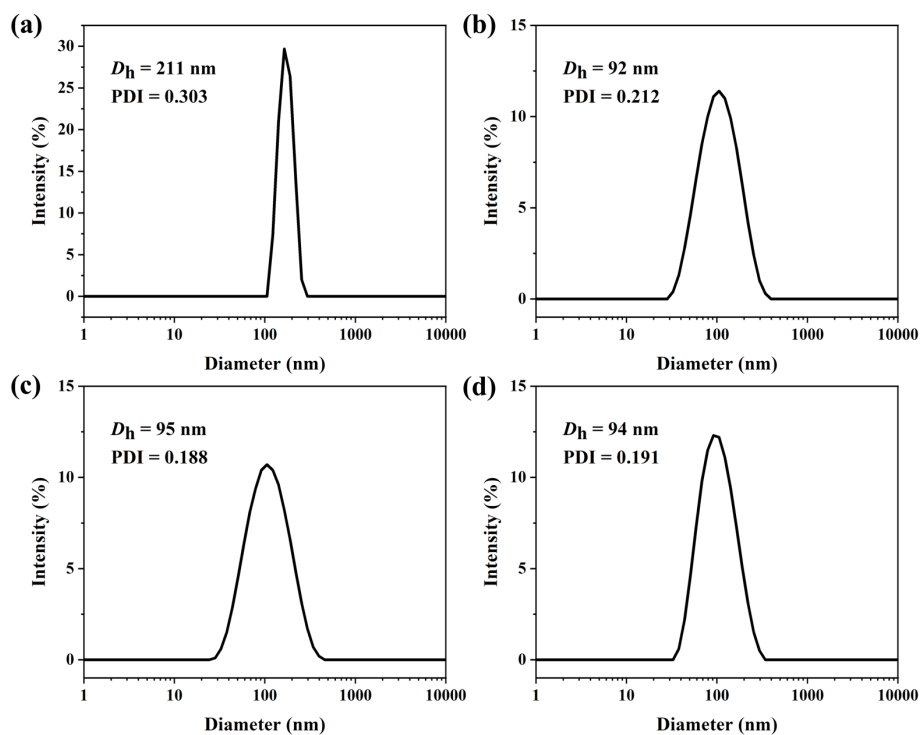


Fig. S14 The effect of pH on the size of PTMCIM-3 polymersomes: (a) pH 7.5, (b) pH 6.5, (c) pH 5.5, and (d) pH 4.5.

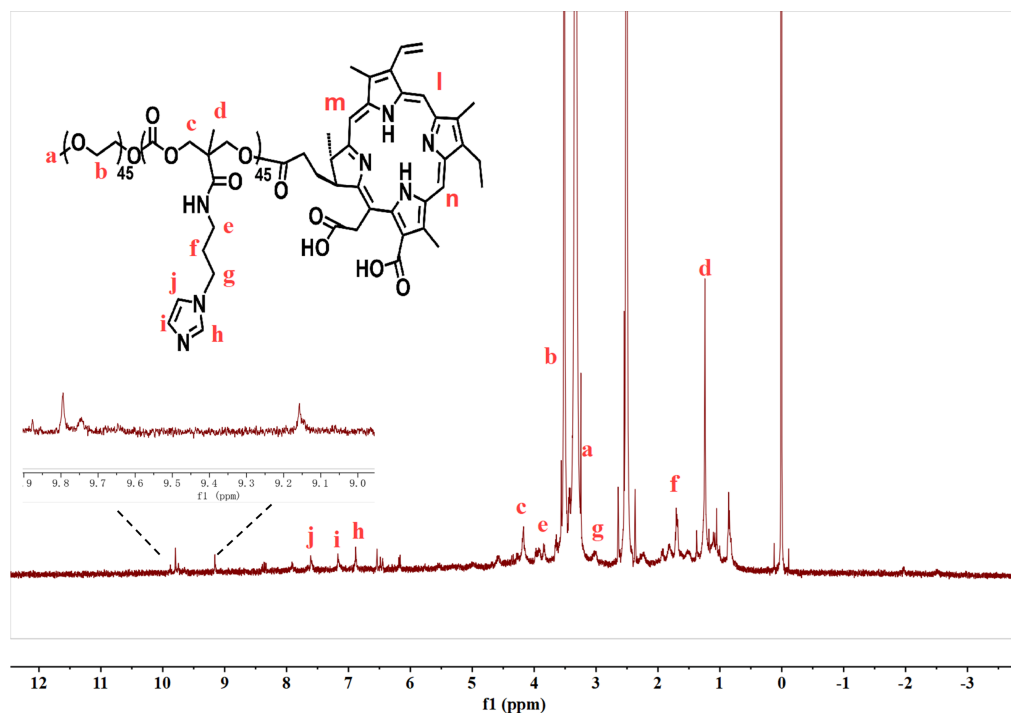


Fig. S15 ^1H NMR spectrum of Ce6 labeled PTMCIM-3 in $\text{DMSO-}d_6$.

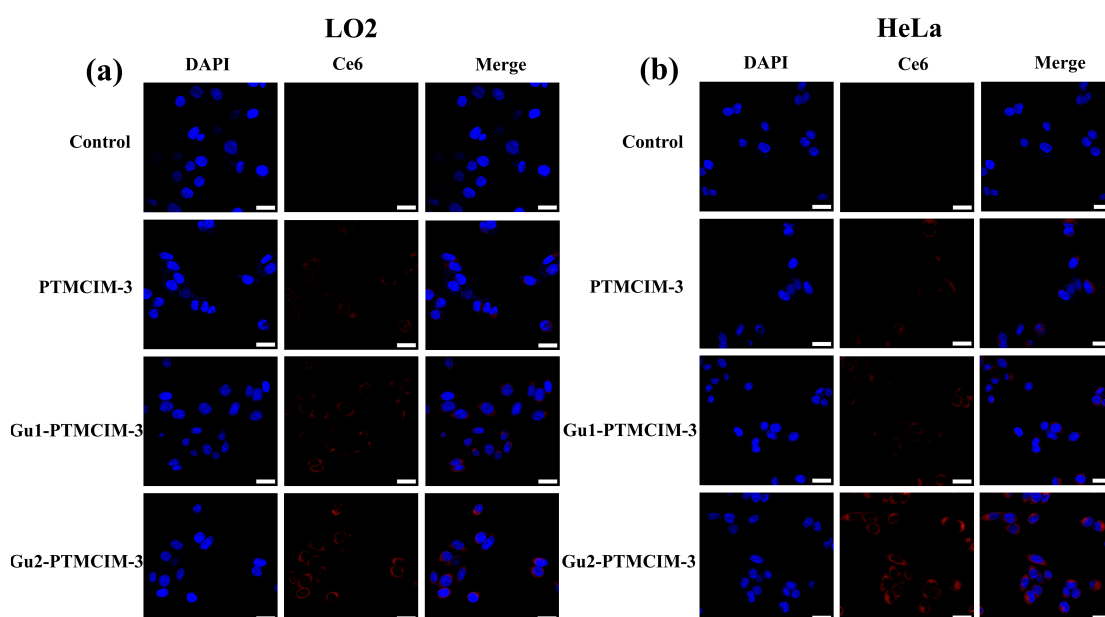


Fig. S16 Polymersome internalization study. CLSM images demonstrated the internalization of Ce6-labeled PTMCIM-3, Gu1-PTMCIM-3 and Gu2-PTMCIM-3 by LO2 cells by (a) LO2 and (b) HeLa cells. Before imaging, the cells were incubated with polymersomes for 6 h. Scale bars are 30 μm .