Electronic Supplementary Material (ESI) for Polymer Chemistry


# Supporting Information

## Intracellular pH-Sensitive Supramolecular Amphiphiles Based on Host-Guest Recognition between Benzimidazole and β-Cyclodextrin as Potential Drug Delivery Vehicle

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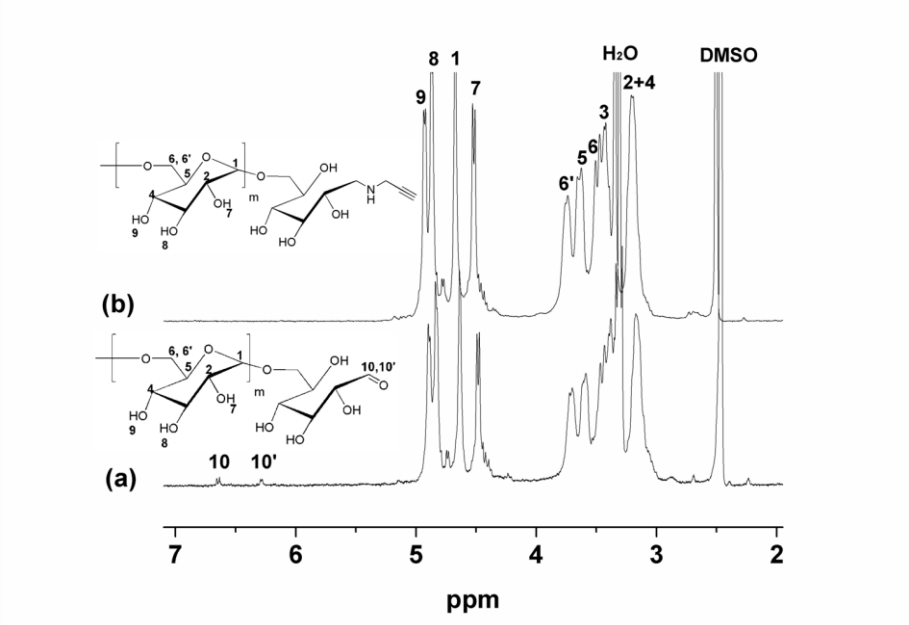


**Fig. S1** $^{1}$H NMR spectra of Dex (a) and α-alkyne Dex (b) in DMSO-$d_6$

$^{1}$H NMR analyses were performed in DMSO-$d_6$ (Fig. S1). The complete disappearance of the anomeric proton peaks of the reducing end group at 6.7 ppm and 6.3 ppm was a strong indication of the quantitative reaction.

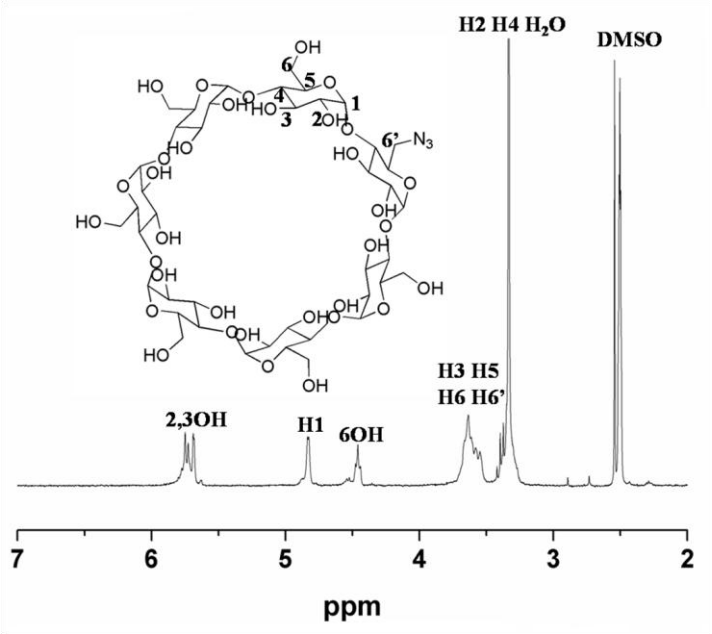


**Fig. S2** $^{1}$H NMR spectrum of mono-6-deoxy-6-azido-β-cyclodextrin (β-CD-$N_3$) in DMSO-$d_6$

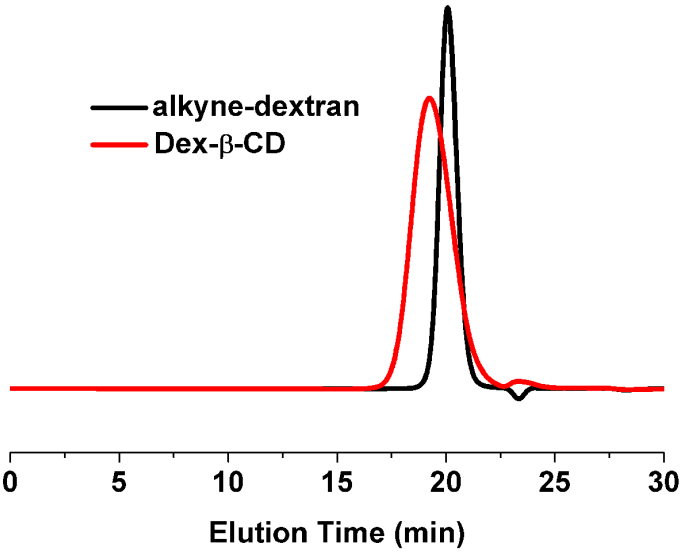


**Fig. S3** Elution time of alkyne dextran and Dex-β-CD in $NaNO_3$ 0.1 M.

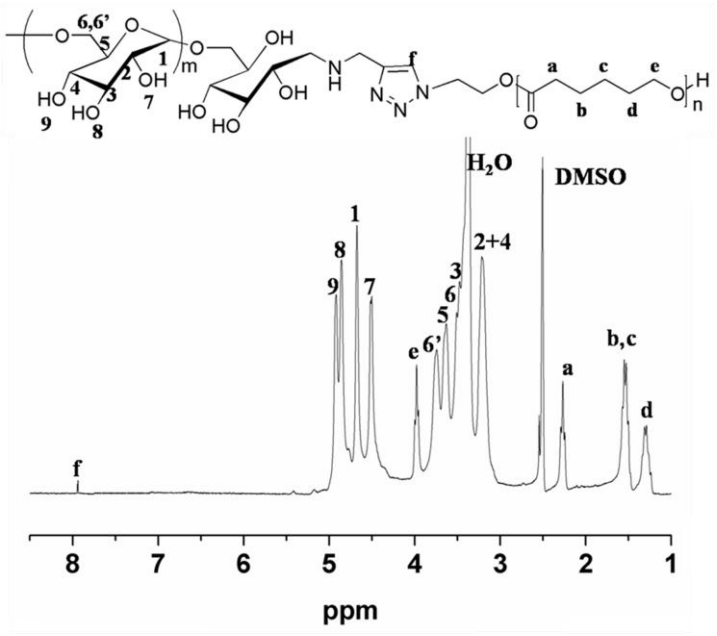


**Fig. S4** $^{1}$H NMR spectrum of Dex-PCL in DMSO-$d_6$

**Table S1** The molecule weight and PDI determined by GPC

| Sample | $M_n$ from GPC | PDI |
|---|---|---|
| α-alkyne Dex | 4600 | 1.24 |
| Dex-β-CD | 6100 | 1.43 |
| Br-PCL | 6800 | 1.28 |
| BM-PCL | 7200 | 1.34 |

**Table S2** DLC and DLE of DOX-loaded Micelles

| Micelles | DLC (wt %) | DLE (wt %) |
|---|---|---|
| Dex-β-CD/BM-PCL | 7.78 | 46.48 |
| Dex-PCL | 8.53 | 51.18 |

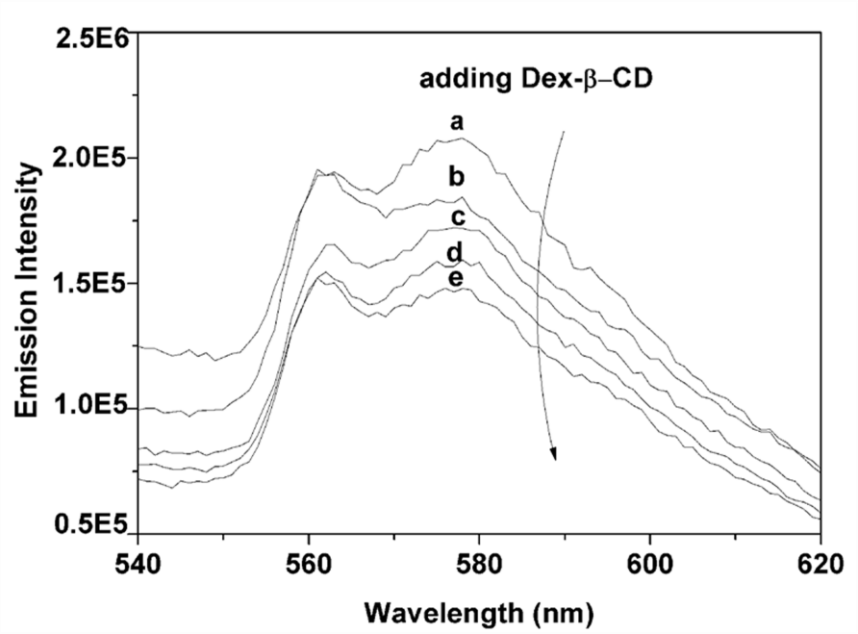


**Fig. S5** Fluorescence emission spectra (540 – 620 nm) of BM-PCL in DMSO/PBS (1:9, v/v) solutions with different Dex-β-CD concentrations ($\lambda_{ex}$ = 240 nm). The concentration of BM-PCL was set at 0.5 mg $mL^{-1}$, while the concentrations of Dex-β-CD were 0 mg $mL^{-1}$ (a), 0.2 mg $mL^{-1}$ (b), 0.8 mg $mL^{-1}$ (c), 1.2 mg $mL^{-1}$ (d) and 1.6 mg $mL^{-1}$ (e).

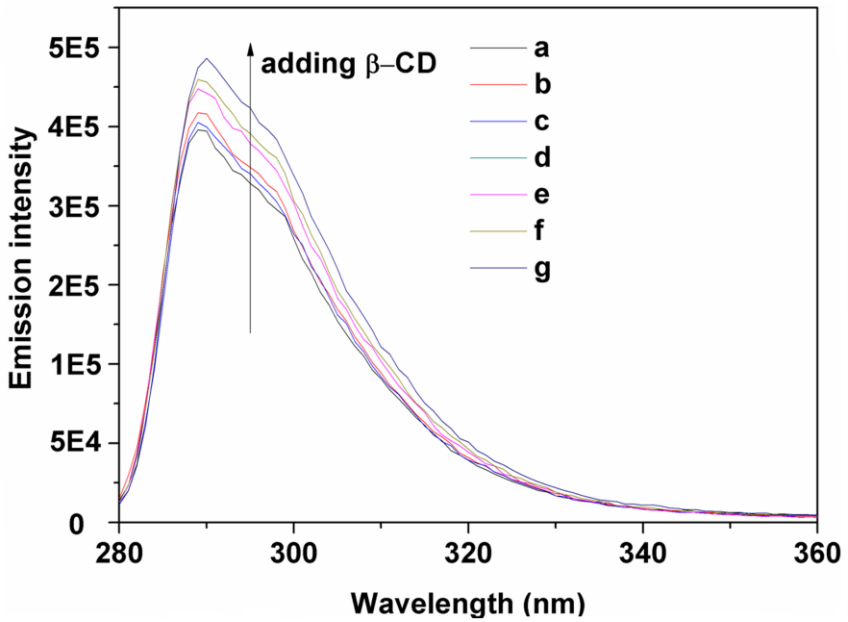


**Fig. S6** Fluorescence emission spectra of BM in DMSO/PBS (1:9, v/v) solutions with different β-CD concentrations ($\lambda_{ex}$ = 240 nm). The concentration of BM was set at 0.5 mg $mL^{-1}$, while the concentrations of β-CD were 0 mg $mL^{-1}$ (a), 0.5 mg $mL^{-1}$ (b), 1.5 mg $mL^{-1}$ (c), 2.5 mg $mL^{-1}$ (d), 5 mg $mL^{-1}$ (e), 10 mg $mL^{-1}$ (f) and 20 mg $ml^{-1}$ (g).

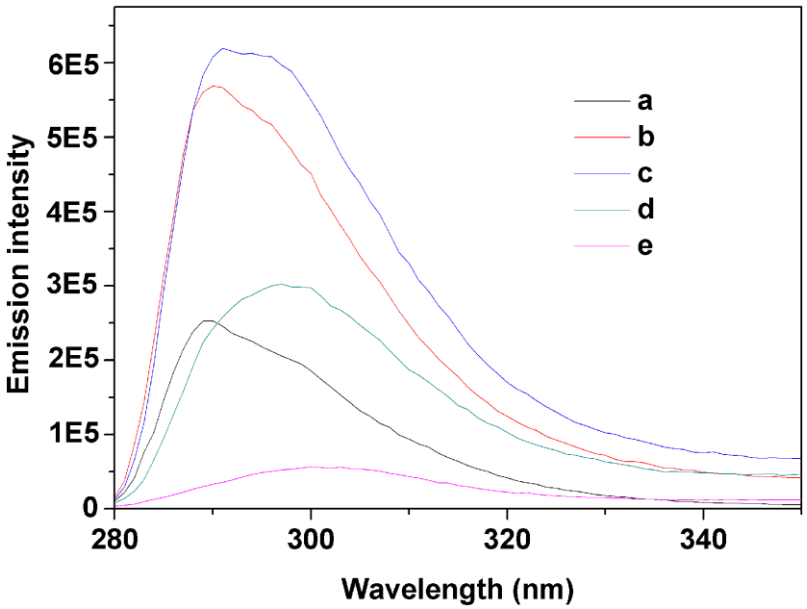


**Fig. S7** Fluorescence emission spectra of BM in DMSO/PBS (1:9, v/v) solutions with different PCL concentrations ($\lambda_{ex}$ = 240 nm). The concentration of BM was set at 0.1 mg $mL^{-1}$, while the concentrations of PCL were 0 mg $mL^{-1}$ (a), 0.5 mg $mL^{-1}$ (b), 1.0 mg $mL^{-1}$ (c), 2.0 mg $mL^{-1}$ (d) and 5.0 mg $mL^{-1}$ (e).

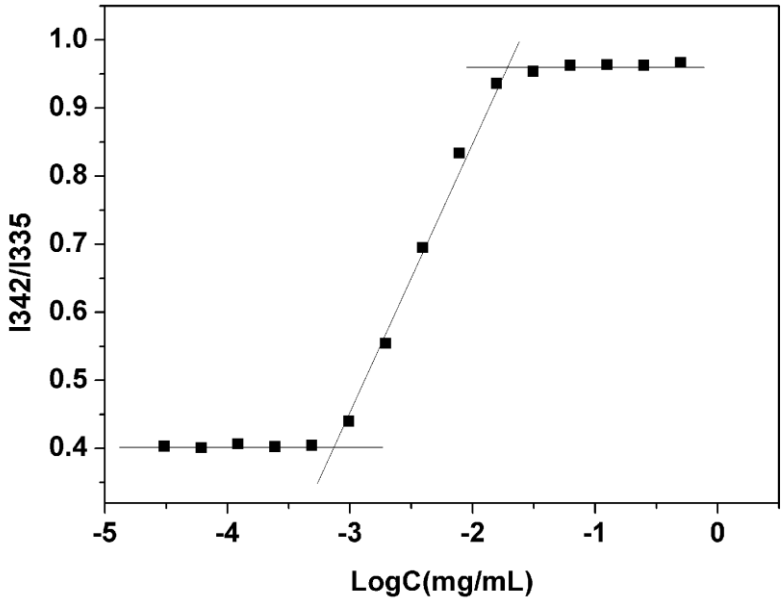


**Fig. S8** Intensity ratios of $I_{342}/I_{335}$ from pyrene excitation spectra as a function of concentration of Dex-PCL copolymer in PBS at pH 7.4. The CMC value of Dex-PCL is 0.71 μg/mL.

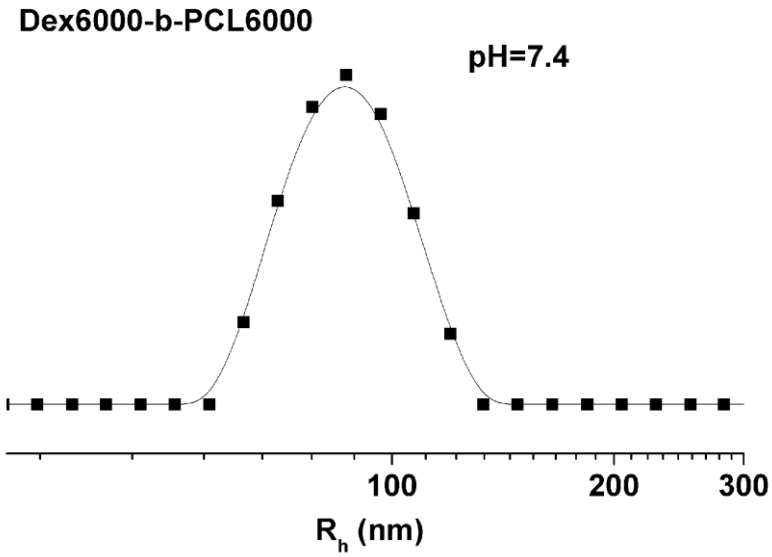


**Fig. S9** The hydrodynamic radii ($R_h$) of Dex-PCL micelles in PBS at pH 7.4.

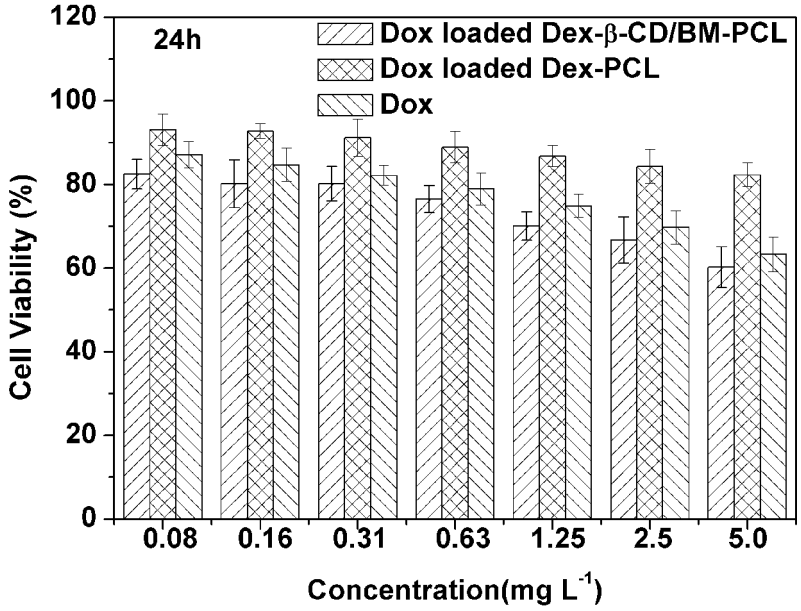


**Fig. S10** Cytotoxicity of DOX-loaded Dex-β-CD/BM-PCL, DOX-loaded Dex-PCL micelles, and free DOX towards HepG2 cells after incubation for 24 h.

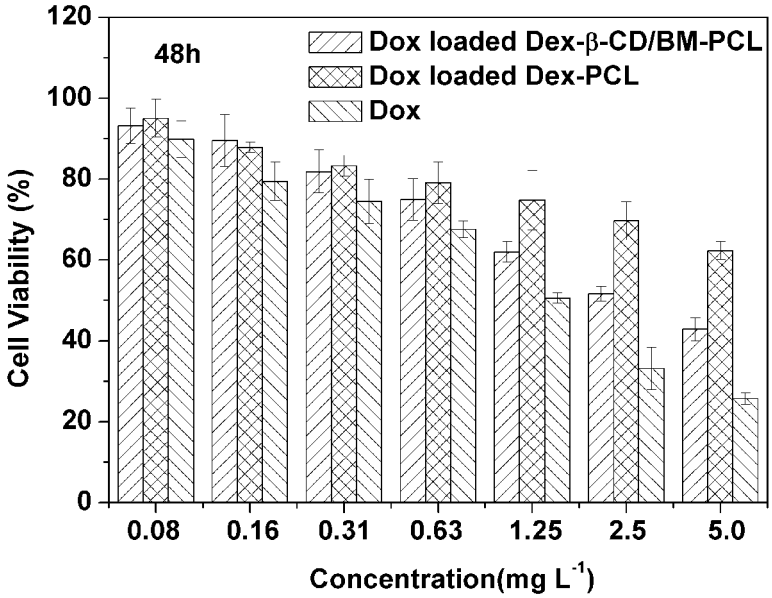


**Fig. S11** Cytotoxicity of DOX-loaded Dex-β-CD/BM-PCL, DOX-loaded Dex-PCL micelles, and free DOX towards HepG2 cells after incubation for 48 h.