† Electronic Supplementary Information (ESI) available:

Facile synthesis of well-defined cyclodextrin-pendant polymer via ATRP for nanostructure fabrication
Mingming Zhang,*‡ Qingqing Xiong,‡ Wei Shen,‡ Qiqing Zhang*‡

a Tianjin Key Laboratory of Biomedical Materials, Institute of Biomedical Engineering, Chinese Academy of Medical Sciences & Peking Union Medical College, Tianjin 300192, P. R. China.

b Institute of Biomedical and Pharmaceutical Technology, Fuzhou University, Fuzhou 350002, P. R. China.

* Corresponding author. E-mail: mingmingz@gmail.com (M. Zhang), zhangqiq@126.com (Q. Zhang). Phone/Fax: +86-22-87890868.

‡ These authors contributed equally to this work.
Synthesis of Mono-6-(p-tolyl sulfonyl)-β-cyclodextrin (mono-6-Ts-CD)

β-CD (180 g, 0.16 mol) was suspended in 1500 mL of distilled water, and 60 mL of NaOH (19.71 g, 0.49 mol) aqueous solution was dropped into the solution. The solution was allowed to cool to 0°C and p-toluenesulfonyl chloride (45.36 g, 0.24 mol) in 135 mL of acetonitrile was dropped in the solution. The reaction mixture was stirred at 23°C for 2 h, and the viscous white precipitate was recovered by centrifugation. The basic supernatant was then neutralized to pH 6.0 by HCl, refrigerated at 4°C overnight and subsequently centrifugated to collect a second precipitate. The combined precipitates were recrystallized twice from water and dried under vacuum to give a white powder (26.6 g, 12.9%). ^1H NMR (DMSO-d$_6$, ppm) (Fig. S1†): 7.7 ppm (2 H, two protons on phenyl group), 7.4 ppm (2 H, two protons on phenyl group), 4.8 ppm (7 H, C1-H on CD rings). ESI-MS (Fig. S2†): m/z 1311.3677 (mono-6-Ts-CD + Na$^+$), calcd 1289.17.

Fig. S1† ^1H NMR spectrum of mono-6-Ts-CD in DMSO-d$_6$.

Fig. S2† The ESI-MS spectrum of mono-6-Ts-CD.
Synthesis of ADA-PDMAEMA homopolymer by ATRP

CuCl (0.0050 g, 0.05 mmol), CuCl₂ (0.0014 g, 0.01 mmol) and bpy (0.0188 g, 0.12 mmol) were dissolved in acetone/water (95/5, v/v) (0.5 mL) in a 10 mL two-neck flask and degassed with three freeze-pump-thaw cycles. A solution of ADA-Br (0.1505 g, 0.05 mmol) and DMAEMA (0.7861 g, 5 mmol) in acetone/water (1.5 mL) was added into the solution through a syringe under Ar atmosphere, and the mixture was degassed with another two freeze-pump-thaw cycles. The reaction mixture was then stirred at 30°C for 20 h. The polymer was further purified by dialysis against deionized water for 48 h and recovered by lyophilization. The conversion of monomer is 58% and the degree of polymerization of DMAEMA is estimated as 58 according to the ¹H NMR result (Fig. S3†). The Mₙ is 14130 with a polydispersity of 1.16 characterized by GPC.

**Fig. 3†** The ¹H NMR spectrum of ADA-PDMAEMA homopolymer in CDCl₃.
**Fig. S4†** The $^1$H NMR spectrum of 6-PA-CD in D$_2$O.

**Fig. S5†** The ESI-MS spectrum of 6-PA-CD.
Fig. S6† The $^1$H NMR spectrum of MCD in DMSO-$d_6$.

Fig. S7† The ESI-MS spectrum of MCD.
**Fig. S8†** GPC spectrum of PEG-\textit{b}-PCD block copolymer (Entry 6). DMF with 0.01 M of LiBr was used as mobile phase at a flow rate of 1.0 mL min\(^{-1}\). Polymer solution was injected through PLgel 10 μm 10\(^3\) Å and 10\(^4\) Å columns at 70°C.

**Fig. S9†** TEM of PEG-\textit{b}-PCD diblock copolymer in aqueous solution. Scale bar: 200 nm.
Fig. S10† GPC spectra of PDMA$_2$/PCD$_{10}$ complex, PDMA$_8$/PCD$_{10}$ complex and PEG-b-PCD block copolymer. 0.15 M Na$_2$SO$_4$ aqueous solution was used as mobile phase at a flow rate of 0.5 mL min$^{-1}$. Polymer solution was injected through Shodex SB-802.5, 803 and 804 HQ columns at 40°C.

Fig. S11† UV-vis spectra of MO in PBS solution, or PBS solution containing β-CD, PEG-b-PCD or PLA$_{0.5}$/PCD$_{10}$ complex.