Electronic Supplementary Information (ESI) for:

Cucurbit[8]uril-based stimuli-responsive films as sacrificial layer for preparation of free-standing thin films

Dan-dan Li, Xia-chao Chen, Ke-feng Ren* and Jian Ji*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China.

E-mail: Jijian@zju.edu.cn, Renkf@zju.edu.cn

Materials and Methods

Materials and Reagents: Poly(ethylenimine) (PEI, branched, Mw = 25 000), poly(arylic acid) (PAA, M w = 100 000 , 35 wt% aqueous solution), poly(sodium 4-styrenesulfonate) (PSS, M w = 70 000), poly(diallyldimethylammonium chloride) (PDDA, Mw = 100 000–200 000, 20wt% aqueous solution), N,N′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), sodium dithionite ($Na_2S_2O_4$) and 2-Adamantylamine hydrochloride (Ad) were purchased from Sigma-Aldrich. Dextran (Mw = 10000), 2-Naphthoxyacetic acid and methyl viologen (MV) were purchased from Aladdin. Cucurbit[8]uril (CB(8)) was supplied by a lab of the University of New South Wales, Australia.[1-3] Ultrapure water obtained from a Millipore water purification system (MilliQ, >18 MΩ, Millipore). All other solvents and reagents were purchased from domestic suppliers and used as received.

Synthesis of the 2-Naphthoxy modified dextran (NpD). 2-Naphthoxyacetic acid (0.202 g, 1 mmol) was activated by DCC (0.227g, 1.1mmol) and a catalytic amount of DMAP in DMSO (10mL) for 30min, then added dextran (0.4g). The reaction mixture was stirred at room temperature for 24 h, and then purified by precipitating in ethyl ether. The resulting yellow product was dried in vacuum overnight, and then characterized by ^{1}HNMR (Bruker DMX500).

Fabrication and disassembly of PAA/MV-CB[8]-NpD Multilayer films. PAA was diluted to 3 mg/mL by ultrapure water. MV-CB[8]-NpD was prepared by dissolving MV, CB[8] and NpD with equal molar concentration of 1 mM in ultrapure water. Multilayer films were built up

by alternating spin coating (3000 rpm, 20s) of PAA and MV-CB[8]-NpD onto substrates, followed by spin-assisted washing two times with ultrapure water. The process was repeated until a desired number of bilayers had been deposited. The disassembly of the multilayer films was performed in $Na_2S_2O_4$ (3 mg/mL) and Ad (3 mg/mL) for a desired time.

Fabrication of free-standing PSS/PDDA multilayer films. PSS/PDDA multilayer films were fabricated onto to the as-prepared PAA/MV-CB[8]-NpD multilayers by using the similar procedure described above. The concentration of PSS and PDDA used for assembly was both 2 mg/mL in ultrapure water. Free-standing PSS/PDDA multilayer films were obtained by disassembly the sacrificial layers PAA/MV-CB[8]-NpD in $Na_2S_2O_4$ (3 mg/mL) or Ad (3 mg/mL) for about 2 min.

Characterization of Multilayers films. The growth of PAA/MV-CB[8]-NpD multilayers on silicon wafers was followed by Spectroscopic ellipsometry (M-2000, J. A. Wollam Co. Inc.). The morphology of the multilayer films was measured by Atomic force microscopy (AFM) (Seiko SPI3800N station, Seiko Instrument Inc., Japan). A field emission scanning electron microscope (FESEM, SIRION-100, FEI, Holland) was used to characterize the cross-section image of the multilayer films. UV-vis spectra were carried out with a UV-vis spectrometer (Shimadzu UV-2505). Digital camera images were captured by using a Sony camera (SONY DSC H50).

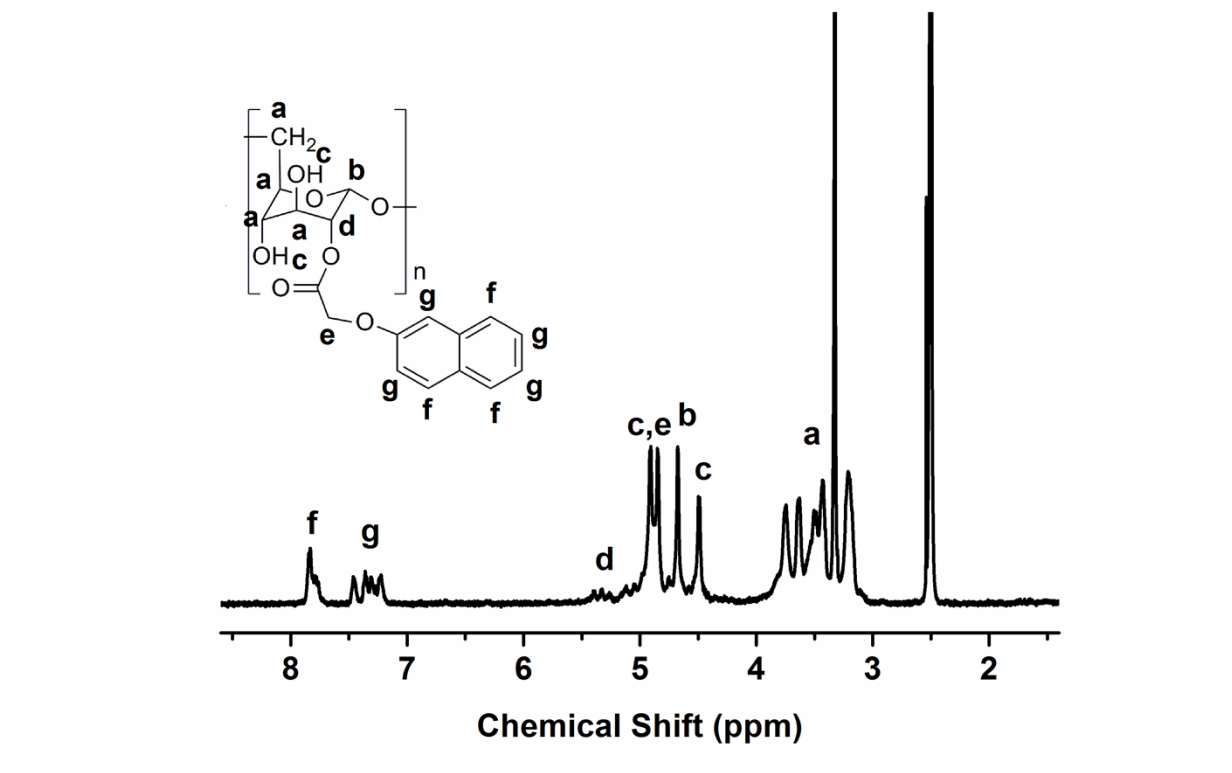

Fig. S1 ^{1}H-NMR spectra of NpD in DMSO-d_6.

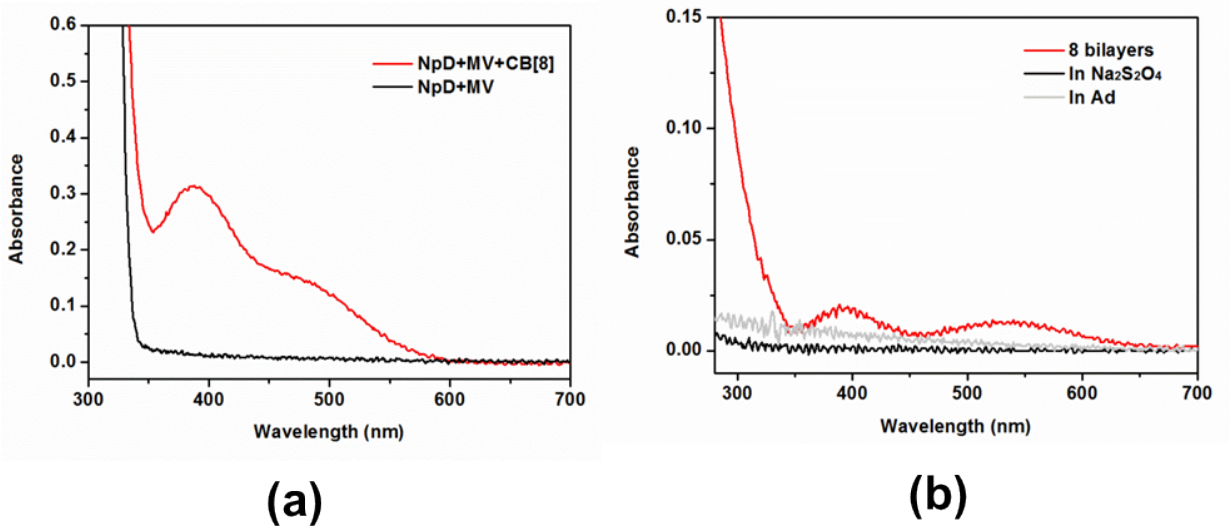

Fig. S2 (a) UV-vis spectra of the solution of equimolar mixture of NpD and MV in the presence (red line) and absence (black line) of 1 equiv of CB[8]. (b) UV-via spectra of the $(PAA/MV\text{-}CB[8]\text{-}NpD)_8$ film (red line), and after immersing in $Na_2S_2O_4$ (black line) and Ad (gray line) solutions.

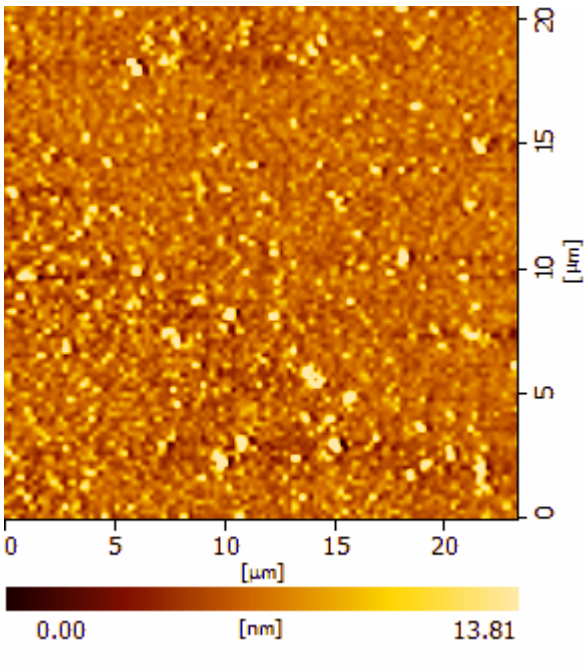

Fig. S3 AFM images of the substrate after the disassembly of the sacrificial layers through immersing in $Na_2S_2O_4$ solutions.

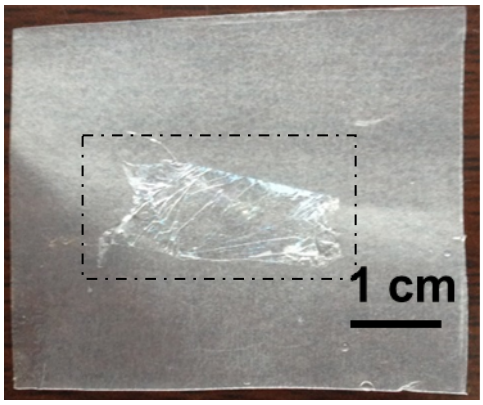

Fig. S4 Photograph of a PLGA free-standing film with a thickness of 237 nm transferred from the silica substrate to a Parafilm.

References

1. A. I. Day, R. J. Blanch, A. P. Arnold, S. Lorenzo, G. R. Lewis and I. Dance, *Angewandte Chemie International Edition*, 2002, **41**, 275-277.
2. A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *The Journal of Organic Chemistry*, 2001, **66**, 8094-8100.
3. N. J. Wheate, D. P. Buck, A. I. Day and J. G. Collins, *Dalton Transactions*, 2006, 451-458.