## Electronic Supplementary Information (ESI)

# Pillararene-based supramolecular membrane with rose-petal effect and nanostructures-modulated tunable water adhesion

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**Synthesis of PCL-*b*-PEG-*b*-PCL.** The ring opening polymerization of ε-caprolactone (ε-CL) (25.1 g, 0.22 mol) used poly(ethylene glycol) (PEG) (10.2 g, 5.0 mmol) with average molecular weight ($M_n$) of 2050 as an initiator and stannous octoate ($Sn(Oct)_2$) (2.02 g, 5.0 mmol) as a catalyst in toluene (50 mL). The reaction solution was stirred at 100 °C under a nitrogen atmosphere for 16 h. After the reaction mixture was cooled to room temperature, the reaction mixture was added dropwise into cold methanol (500 mL). The mixture was filtered and the filter cake was dried in vacuum to give product (yield: 75.0%) as white solid. $^1$H NMR (400 MHz, $CDCl_3$, δ): 4.06 (t, 83H, $CH_2$), 3.65 (s, 184H, $CH_2$), 2.31 (t, 83H, $CH_2$), 1.65 (m, 180H, $CH_2$), 1.38 (m, 88H, $CH_2$).

**Synthesis of DEP5A.** A solution of 1,4-diethoxybenzene (8.3 g, 50.0 mmol), paraformaldehyde (4.5 g, 150.0 mmol) and boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) (7.1 g, 50.0 mmol) in dichloromethane (400 mL) were added into a 1000 mL three-necked round bottom flask. Then the reaction solution was stirred at 30 °C under a nitrogen atmosphere for 15 min. An aqueous solution of $NaHCO_3$ (400 mL) was added into the reaction mixture. The organic layer was separated, dried over $Na_2SO_4$ and evaporated to dryness. The crude product was purified by silica gel chromatography eluted with $CHCl_3$: PE = 3: 1 to give product (yield: 70.0%) as white solid. $^1$H NMR (400 MHz, $CDCl_3$, δ): 6.72 (s, 10H, Ar H), 3.83 (q, 20H, $CH_2$), 3.77 (s, 10H, $CH_2$), 1.26 (t, 30H, $CH_3$).

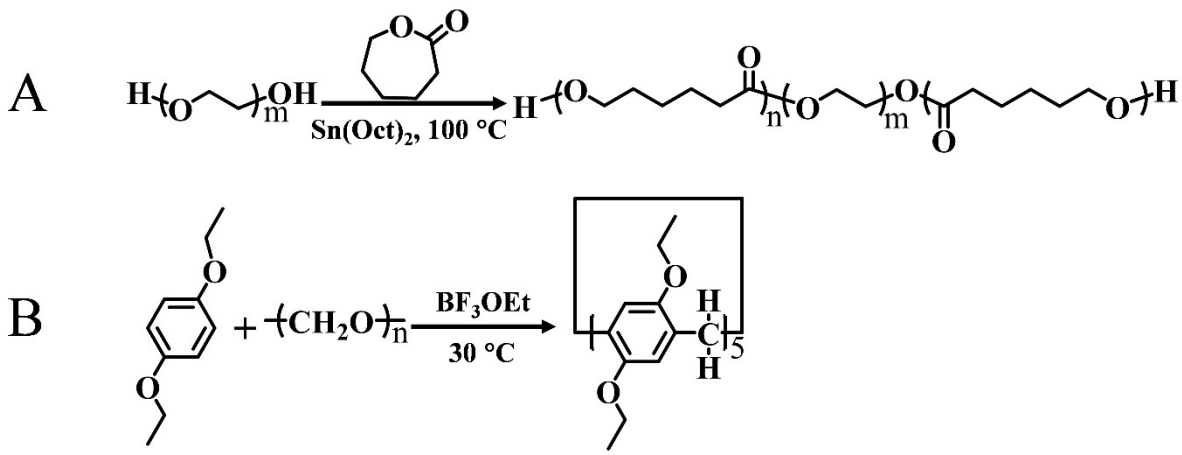


**Fig. S1.** Synthetic routes of PCL-*b*-PEG-*b*-PCL and DEP5A.

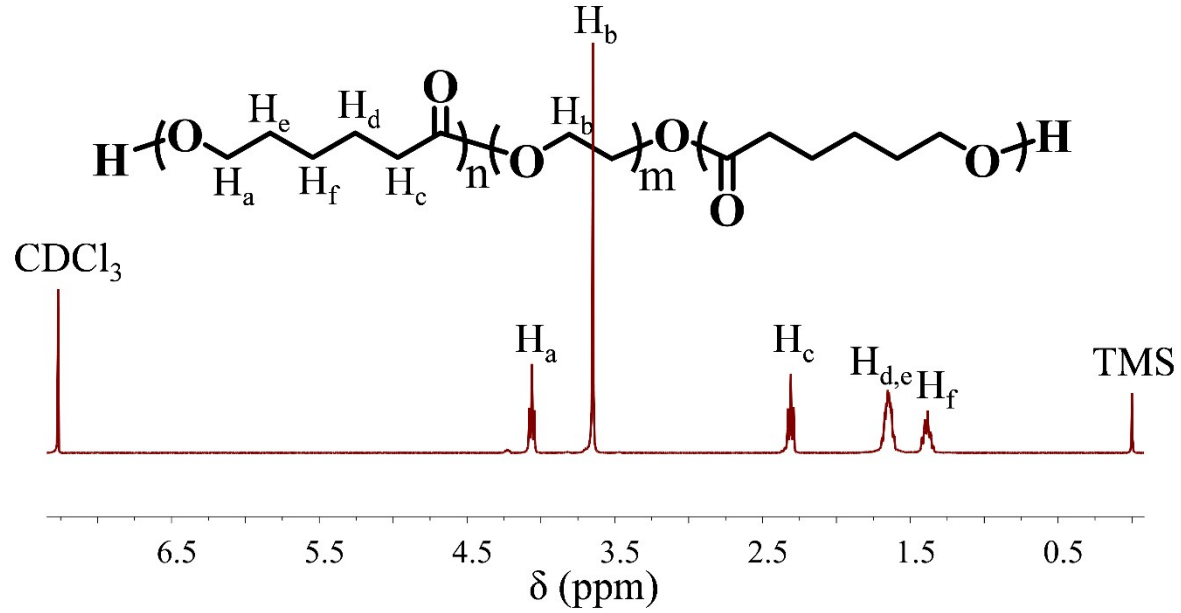


**Fig. S2.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of PCL-*b*-PEG-*b*-PCL (10.0 mg $mL^{-1}$).

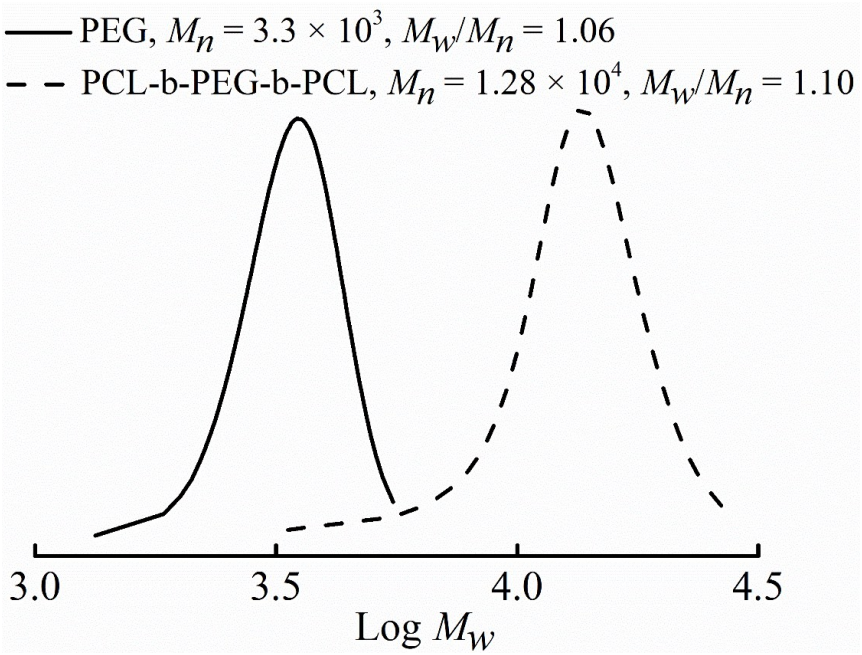


**Fig. S3.** GPC traces of PEG and PCL-*b*-PEG-*b*-PCL.

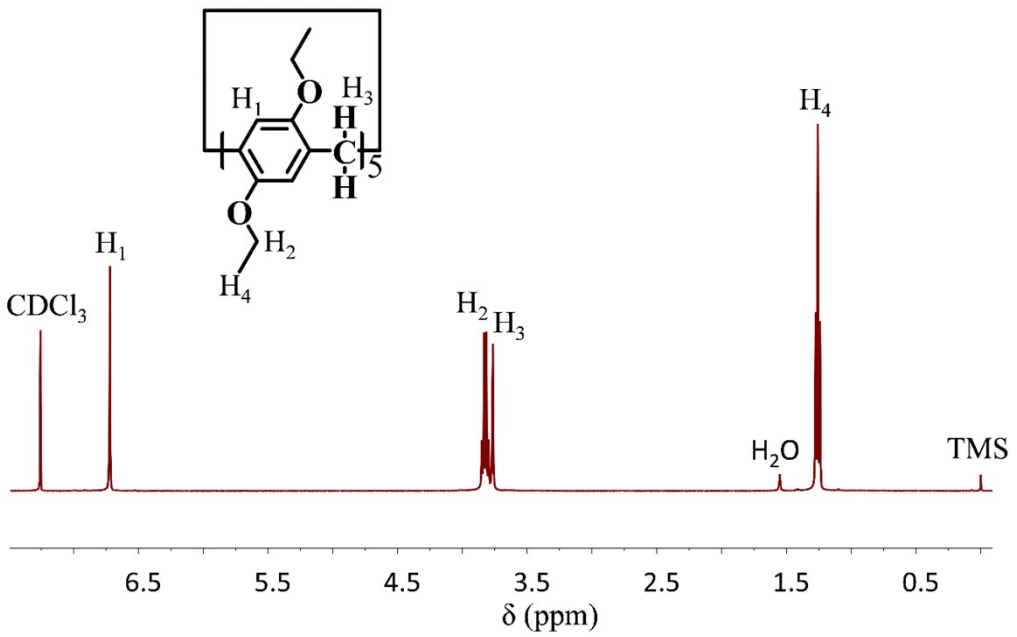


**Fig. S4.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of DEP5A (8.0 mg $mL^{-1}$).

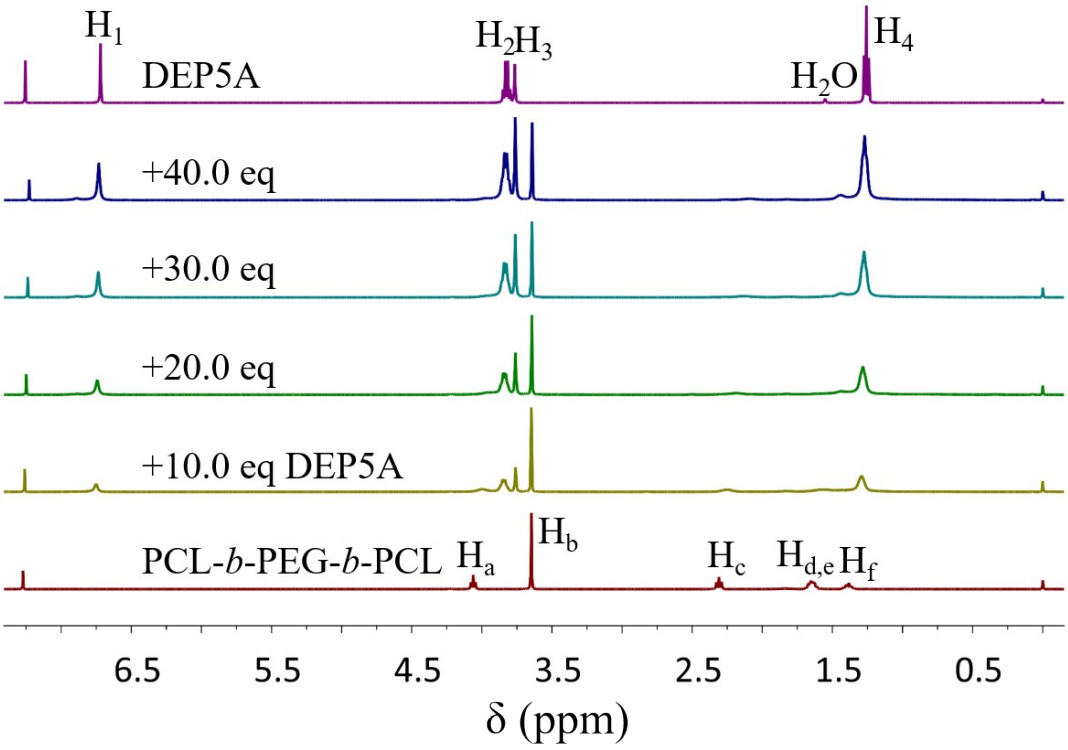


**Fig. S5.** $^{1}$H NMR spectra (400 MHz, $CDCl_3$, 20 °C) of PCL-*b*-PEG-*b*-PCL (10.0 mg $mL^{-1}$) upon the addition of DEP5A.

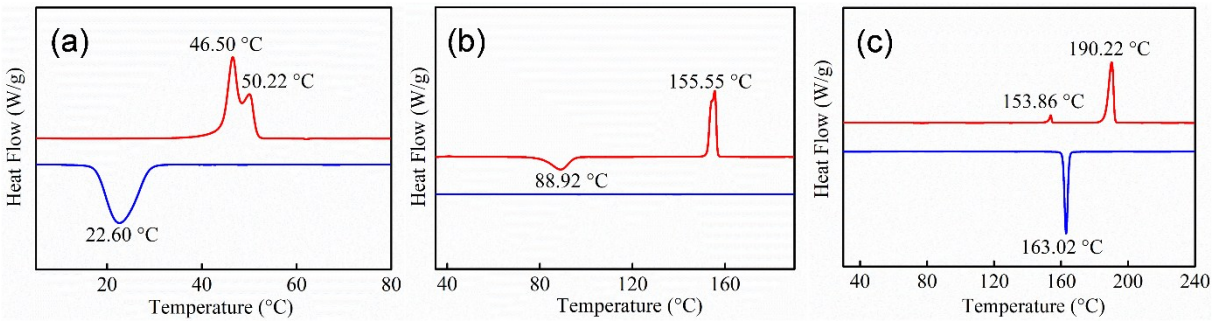


**Fig. S6.** Differential scanning calorimetry (DSC) curves of (a) PCL-*b*-PEG-*b*-PCL, (b) DEP5A, and (c) PPR (40 eq DEP5A).

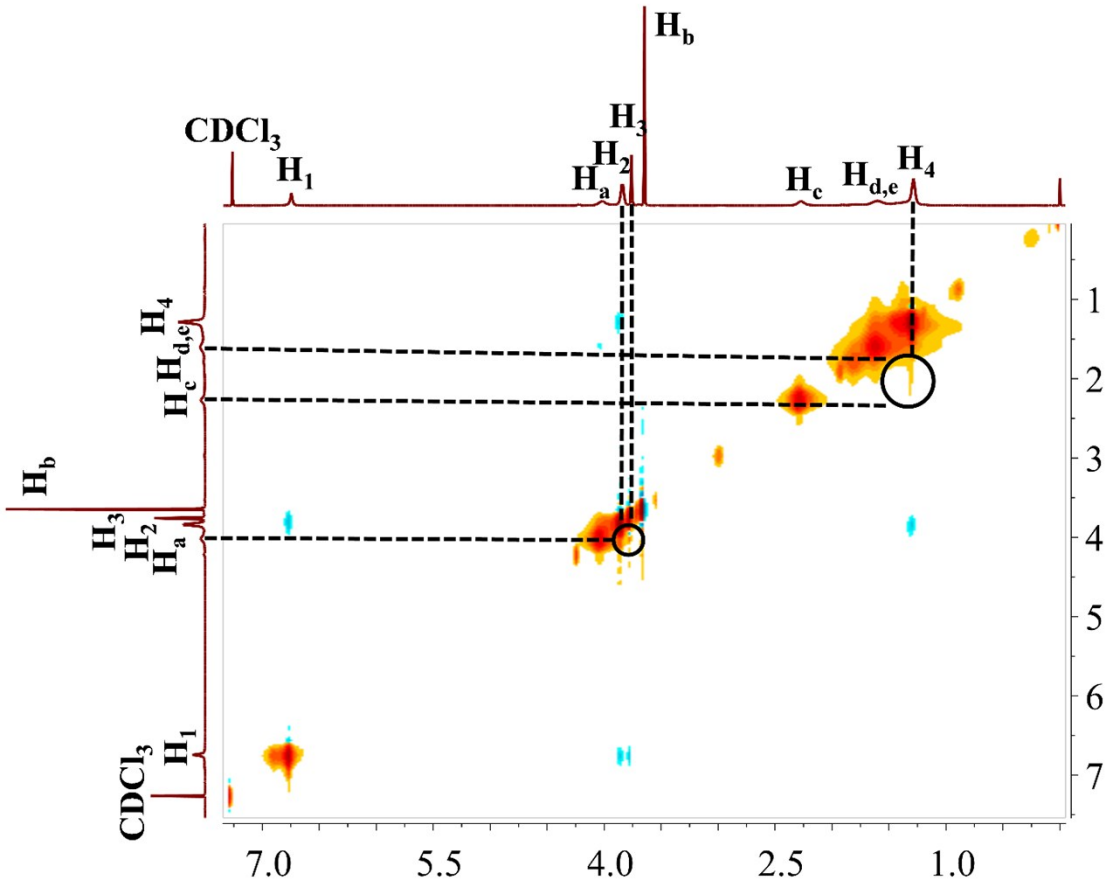


**Fig. S7.** 2D NOESY study of PPR (PCL-*b*-PEG-*b*-PCL (10.0 mg $mL^{-1}$, 1.42 mmol), DEP5A (10 eq)) (600 MHz, $CDCl_3$, 20 °C).

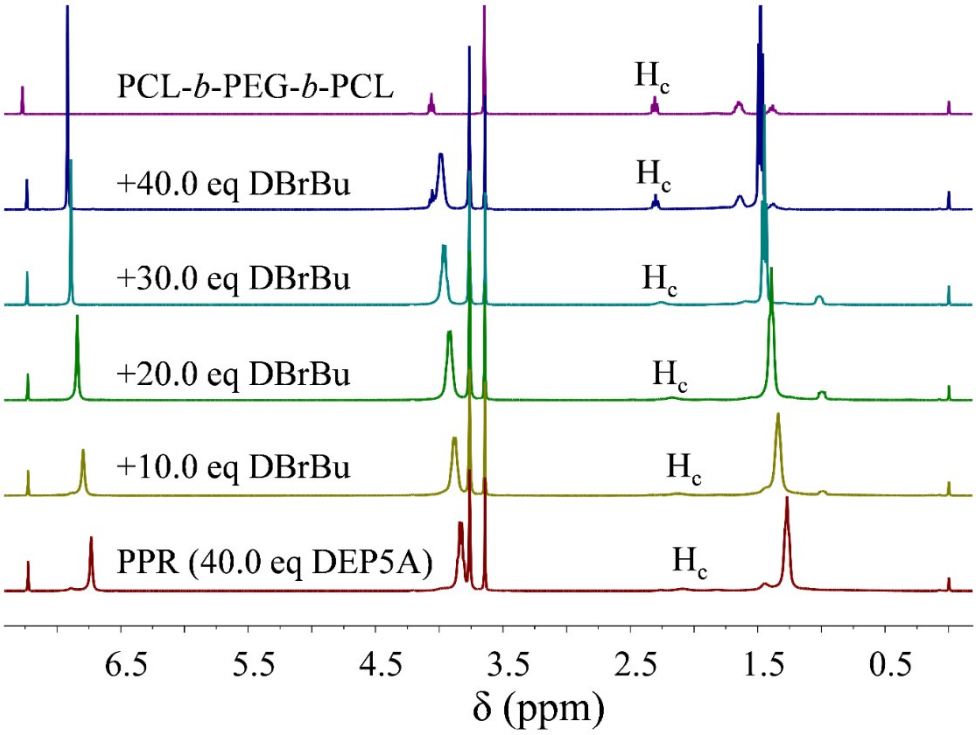


**Fig. S8.** $^{1}$H NMR spectra (400 MHz, $CDCl_3$, 20 °C) of PPR (40.0 eq DEP5A) upon the addition of DBrBu.

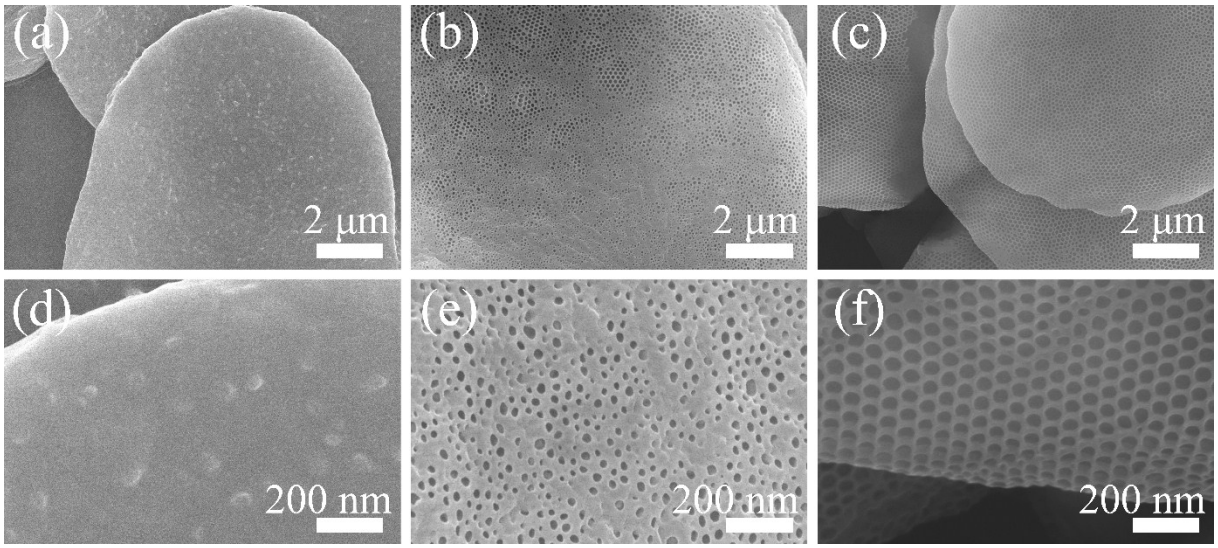


**Fig. S9.** SEM images of nanosheet fabricated under different relative humidity (other conditions remain unchanged): (a) 40% RH; (b) 75% RH; (c) 90% RH. (d), (e), and (f) are the magnified pictures of (a), (b), and (c), respectively. The scale bar of (a), (b), and (c) is 2 $\mu$m; The scale bar of (d), (e), and (f) is 200 nm.

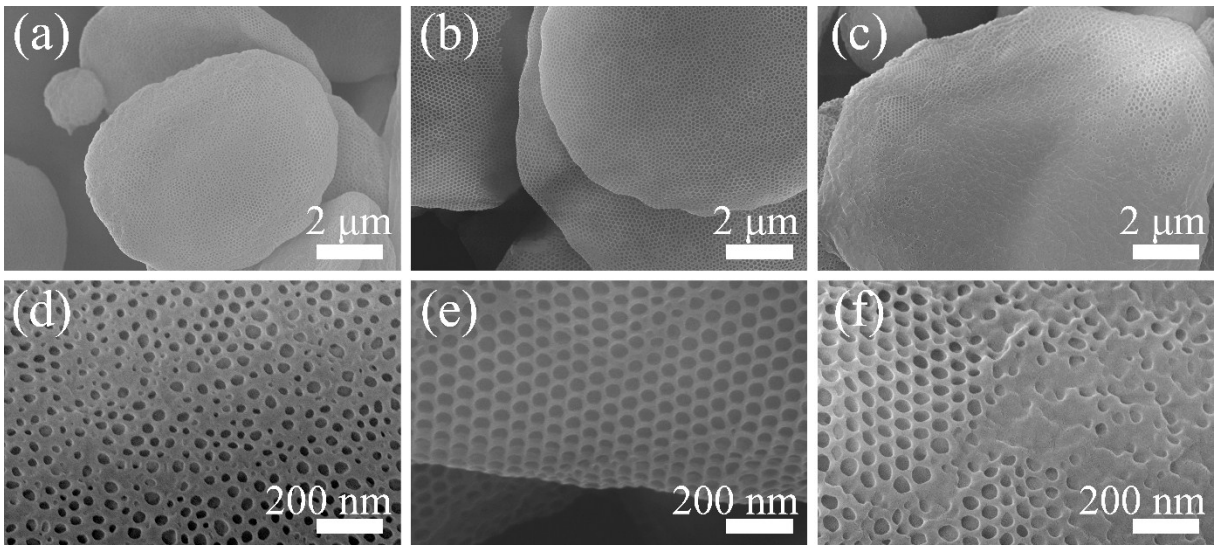


**Fig. S10.** SEM images of nanosheet fabricated under different molar ratios of DEP5A to PCL-*b*-PEG-*b*-PCL (other conditions remain unchanged): (a) 10 eq; (b) 15 eq; (c) 20 eq. (d), (e), and (f) are the magnified pictures of (a), (b), and (c), respectively. The scale bar of (a), (b), and (c) is 2 $\mu$m; The scale bar of (d), (e), and (f) is 200 nm.

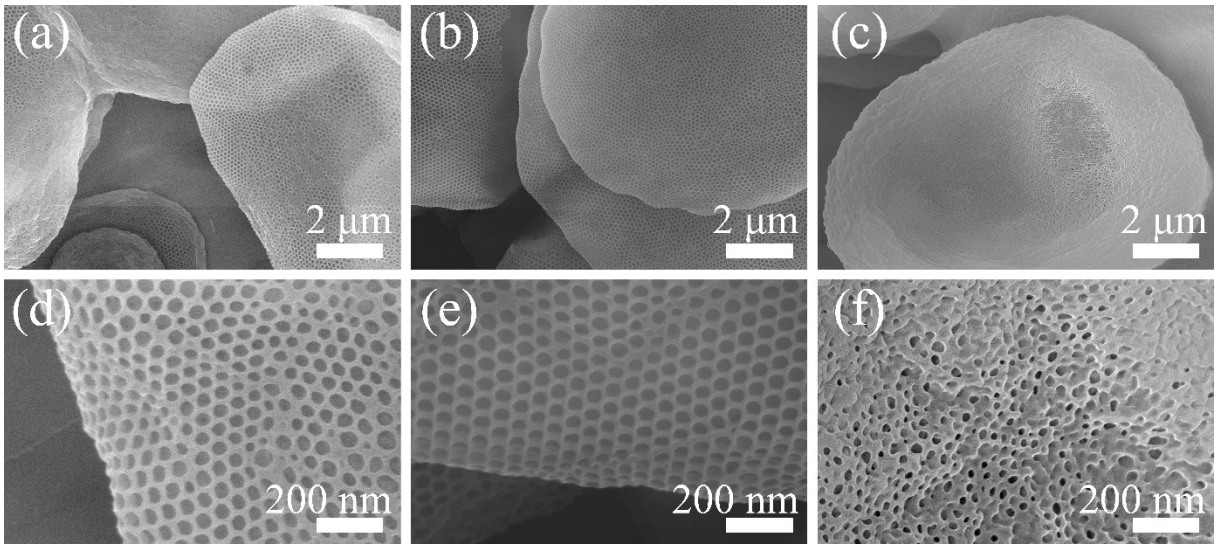


**Fig. S11.** SEM images of nanosheet fabricated under different concentration (other conditions remain unchanged): (a) 5 mg $mL^{-1}$; (b) 10 mg $mL^{-1}$; (c) 15 mg $mL^{-1}$. (d), (e), and (f) are the magnified pictures of (a), (b), and (c), respectively. The scale bar of (a), (b), and (c) is 2 $\mu$m; The scale bar of (d), (e), and (f) is 200 nm.

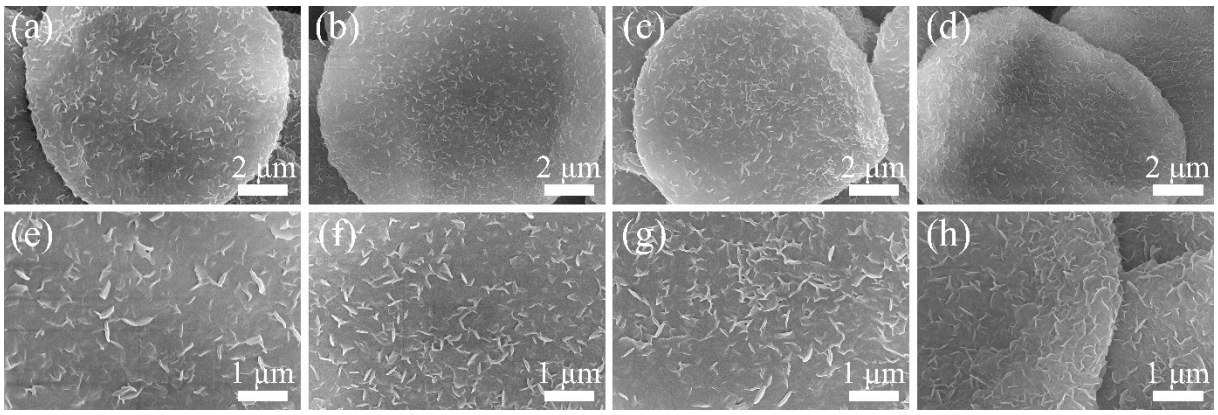


**Fig. S12.** SEM images of FNM fabricated from HNM being immersed in 100 mL ethanol for different times: (a) 10 s; (b) 30 s; (c) 1 min; (d) 10 min. (e), (f), (g), and (h) are the magnified pictures of (a), (b), (c), and (d) respectively. The scale bar of (a), (b), (c), and (d) is 2 $\mu$m; The scale bar of (e), (f), (g), and (h) is 1 $\mu$m.

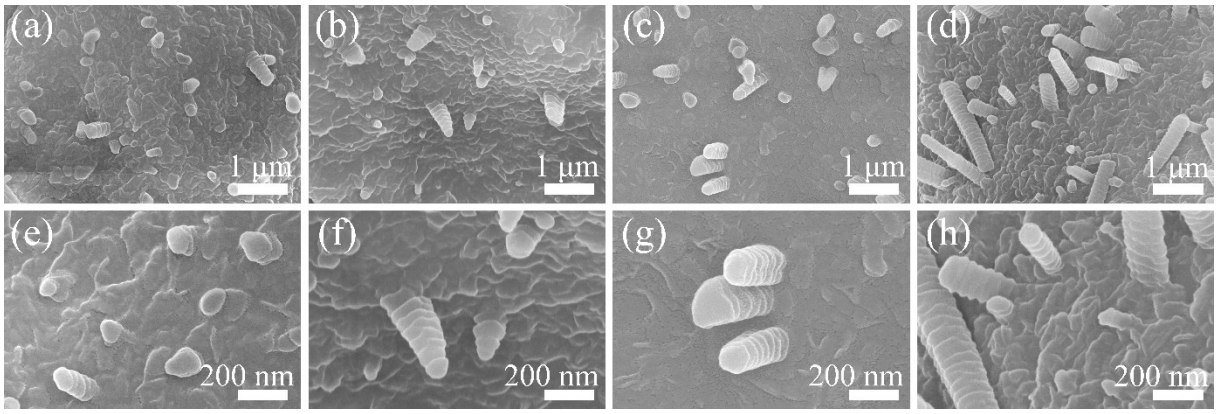


**Fig. S13.** SEM images of PNM fabricated from HNM being immersed in 100 mL ethanol+20 $\mu$L DBrBu for different times: (a) 10 s; (b) 30 s; (c) 1 min; (d) 10 min; and then immersed in 100 mL ethanol for 30 s. (e), (f), (g), and (h) are the magnified pictures of (a), (b), (c), and (d) respectively. The scale bar of (a), (b), (c), and (d) is 1 $\mu$m; The scale bar of (e), (f), (g), and (h) is 200 nm.

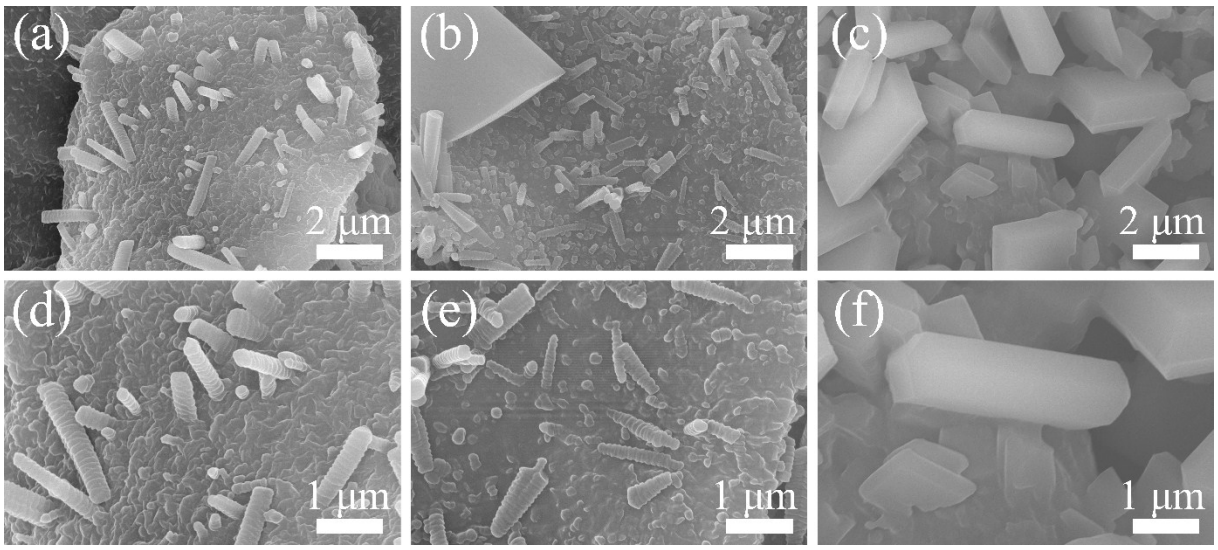


**Fig. S14.** SEM images of PNM fabricated from HNM being immersed in different concentration of DBrBu solution for 10 min: (a) 100 mL ethanol+20 $\mu$L DBrBu; (b) 100 mL ethanol+50 $\mu$L DBrBu; (c) 100 mL ethanol+100 $\mu$L DBrBu; and then immersed in 100 mL ethanol for 30 s. (d), (e), and (f) are the magnified pictures of (a), (b), and (c), respectively. The scale bar of (a), (b), and (c) is 2 $\mu$m; The scale bar of (d), (e), and (f) is 1 $\mu$m.

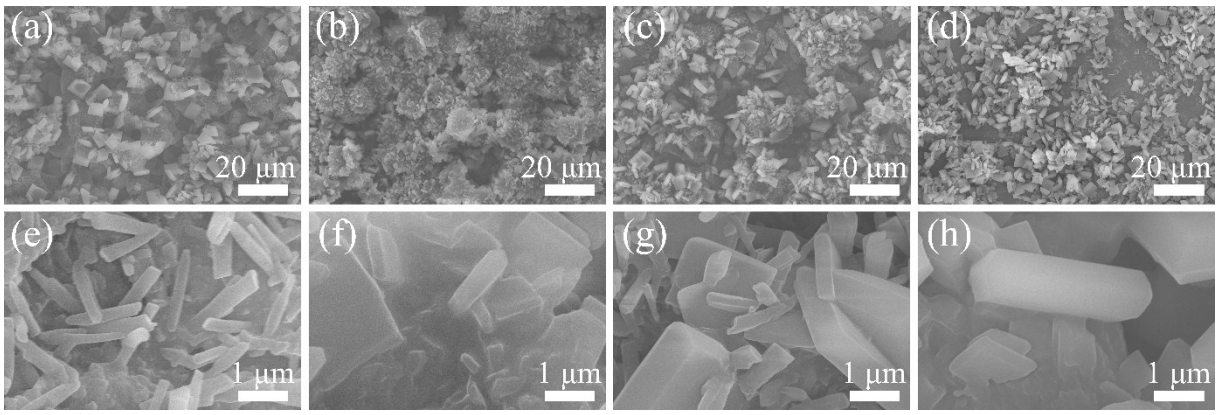


**Fig. S15.** SEM images of PNM fabricated from HNM being immersed in 100 mL ethanol+100 $\mu$L DBrBu for different times: (a) 10 s; (b) 30 s; (c) 1 min; (d) 10 min; and then immersed in 100 mL ethanol for 30 s. (e), (f), (g), and (h) are the magnified pictures of (a), (b), (c), and (d) respectively. The scale bar of (a), (b), (c), and (d) is 20 $\mu$m; The scale bar of (e), (f), (g), and (h) is 1 $\mu$m.