

**Amphiphobic fluorinated polyurethane composite microfibrrous membranes  
with robust waterproof and breathable performances**

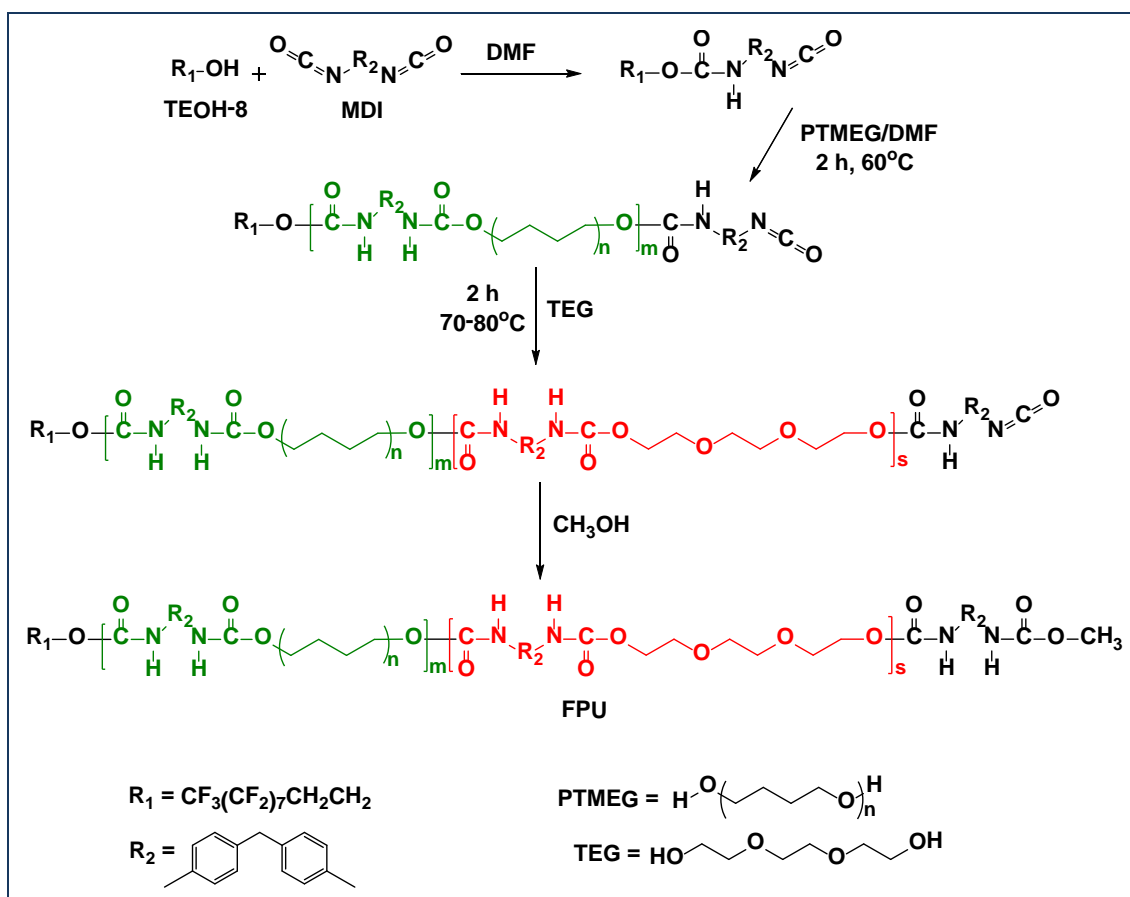
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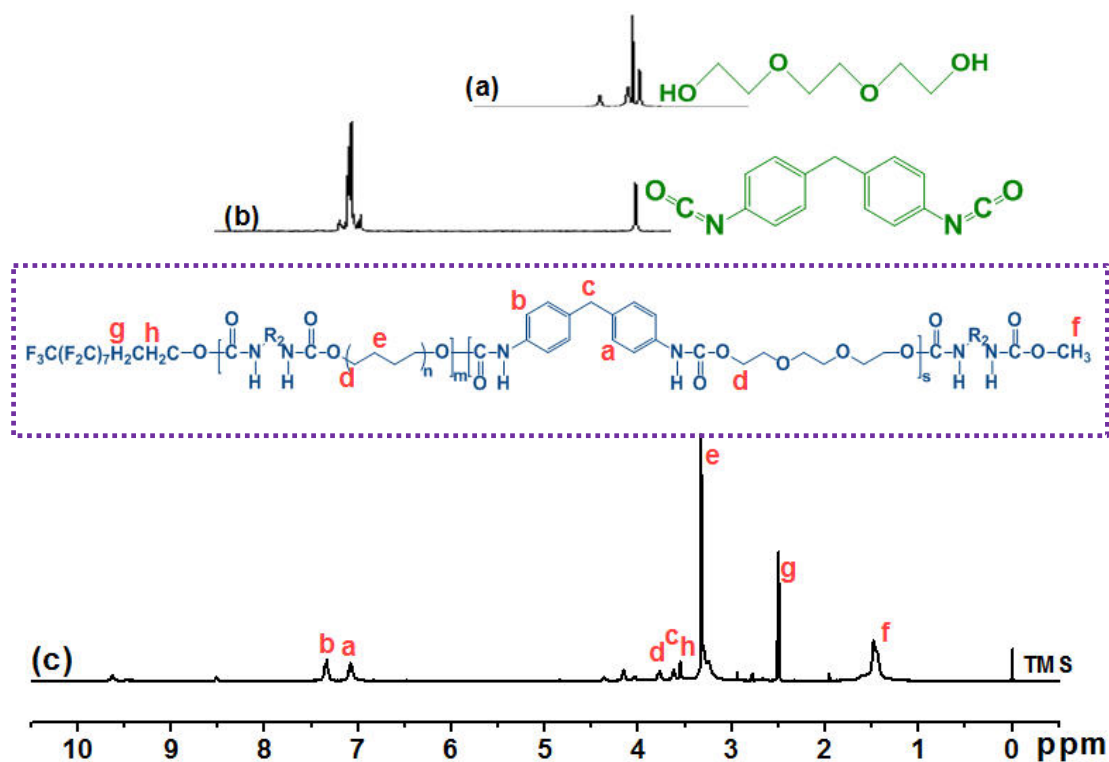
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**Fig. S1** Chemical synthetic and polymerization routes of FPU.

## <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopic analysis

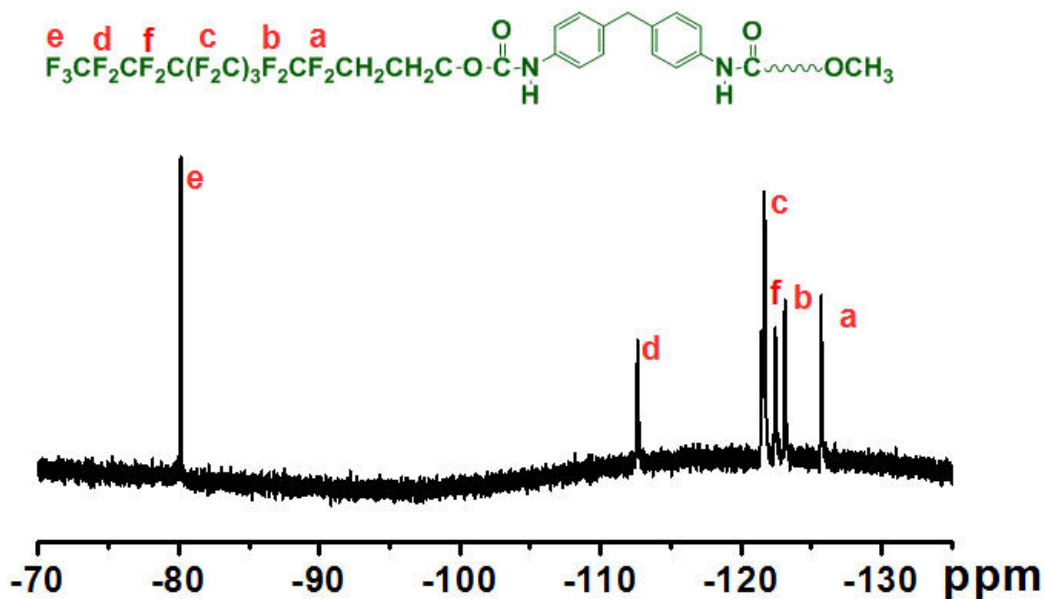


**Fig. S2** <sup>1</sup>H NMR spectrograph of (a) TEG, (b) MDI and (c) FPU.

The as-synthesized FPU after purification and crystallization was subjected to nuclear magnetic resonance (NMR) spectroscopic analysis. Figure S1 illustrates the <sup>1</sup>H NMR spectrum of FPU. For pure TEG, the chemical shifts for -CH<sub>2</sub>- and -OH appeared between 3.60 to 3.72 ppm and around 4.01 ppm, respectively. In case of pure MDI the signals for aromatic protons appeared between 6.90 to 7.16 ppm and for -CH<sub>2</sub>- appeared at 3.89 ppm (Fig. S2a and b). For FPU, the chemical shift for terminal -CH<sub>3</sub>, -CF<sub>2</sub>-CH<sub>2</sub>- and -CH<sub>2</sub>-CH<sub>2</sub>-O appeared at 1.45, 2.53 and 3.52 ppm, respectively. The aromatic protons of the MDI in FPU have given their chemical shift between 7.13 to 7.48 ppm. Comparing to the <sup>1</sup>H NMR of TEG the protons of O-CH<sub>2</sub>-CH<sub>2</sub>-O

have given their signal at 3.78 ppm, and protons of PTMEG have given a sharp signal at 3.34 ppm.

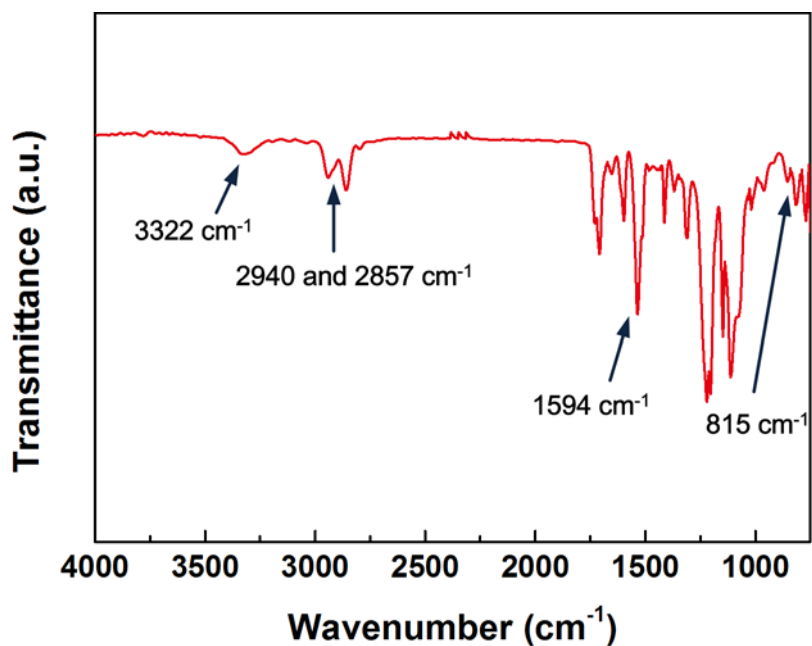
### <sup>19</sup>F NMR spectroscopic analysis



**Fig. S3** <sup>19</sup>F NMR spectrograph of FPU.

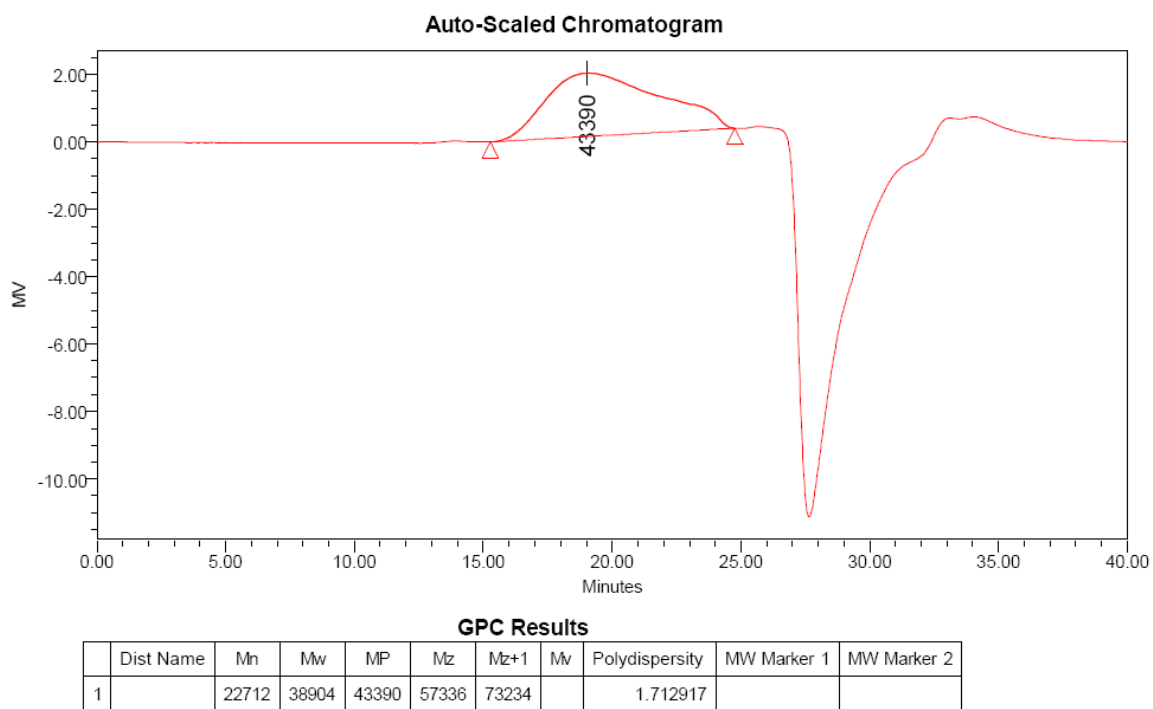
<sup>19</sup>F NMR has given further structural affirmation of FPU (Fig. S3). The chemical shift for terminal -CF<sub>3</sub> appeared at 80.13 ppm, while for -CF<sub>2</sub>-CH<sub>2</sub>- appeared at 125.67 ppm. The remaining -CF<sub>2</sub>- has given their chemical shift between 112.61 to 123.10 ppm. Acquisition of quantitative results from NMR analysis has confirmed the chemical structure of FPU.

### Functional group affirmation of FPU by FT-IR spectroscopy analysis

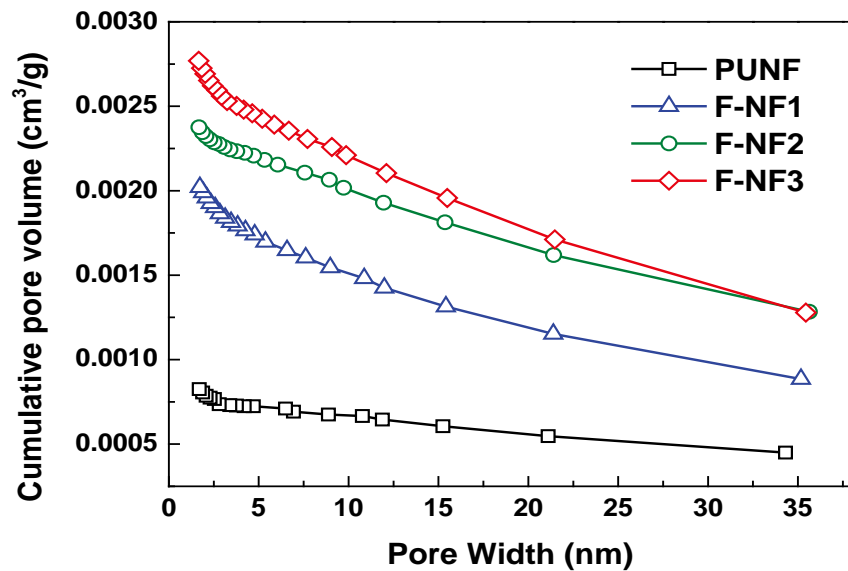


**Fig. S4** FT-IR spectrum of FPU.

Fig. S4 shows the comparative FT-IR spectrum of FPU. The typical absorption features for carbamate group were found at 3322 cm<sup>-1</sup> (-N-H), 1708 cm<sup>-1</sup> (C=O), and 1112 cm<sup>-1</sup> (C-O-C), respectively. The -CH<sub>2</sub>- specific for PTMEG has given their absorption band around 2940 and 2857 cm<sup>-1</sup>. The stretching vibrations for aromatic ring of MDI and terminal CF<sub>3</sub> and deformation vibration for -CF<sub>2</sub>- appeared at 1594 and 815 cm<sup>-1</sup>, respectively.



**Fig. S5** GPC curve of as-synthesized FPU and relevant molecular weight and distribution results.



**Fig. S6** The BJH desorption cumulative pore volume curves of relevant PUNF, F-NF1, F-NF2 and F-NF3 membranes.