A Cost-effective Strategy for Surface Modification via Complexation of Disassembled Polydopamine with Fe(III) Ions

Peibin Zhang[†⊥], *Wenjihao Hu*[‡⊥], *Min Wu*[‡], *Lu Gong*[‡], *Anqi Tang*[†], *Li Xiang*[‡], *Baoku Zhu*[†], *Liping Zhu* [†*], *and Hongbo Zeng*[‡*]

[†] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, PR. China.

[‡] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, T6G 1H9, Alberta, Canada.

* Email: lpzhu@zju.edu.cn or hongbo.zeng@ualberta.ca

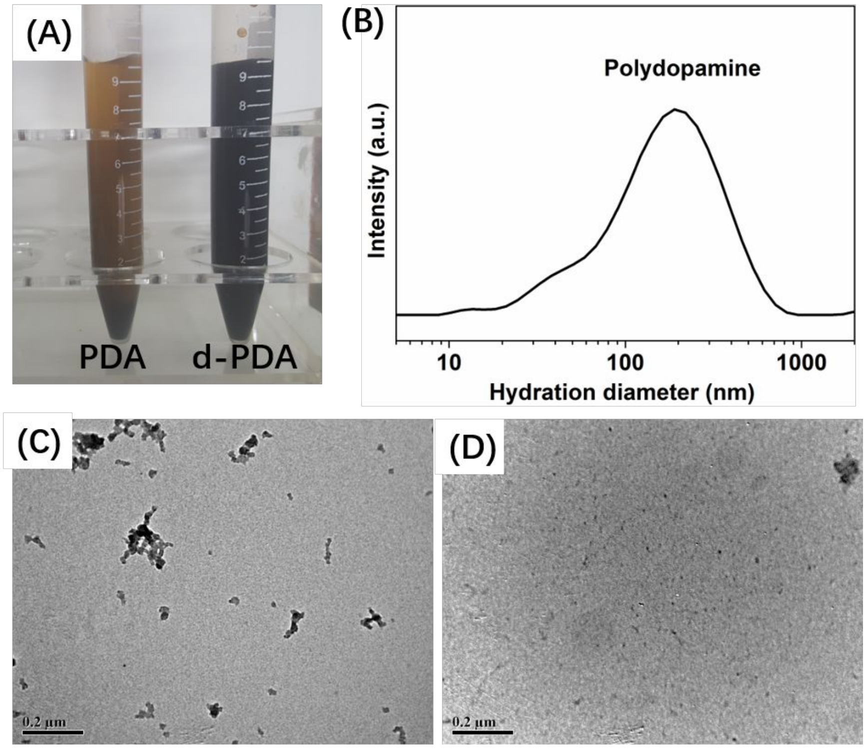

Figure S1. (A) Photo images of polydopamine (PDA) and disassembled polydopamine (d-PDA) solution after centrifugation. (B) Hydration diameter of PDA solution measured by DLS. (C) TEM images of PDA, and (D) d-PDA.

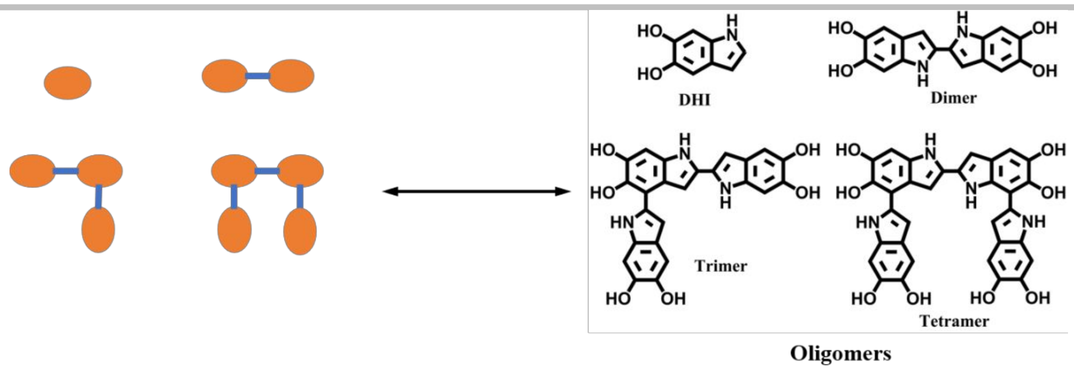

Figure S2. Some typical DHI-based oligomers, which are relatively more favorable formed calculated from theoretical simulations[1].

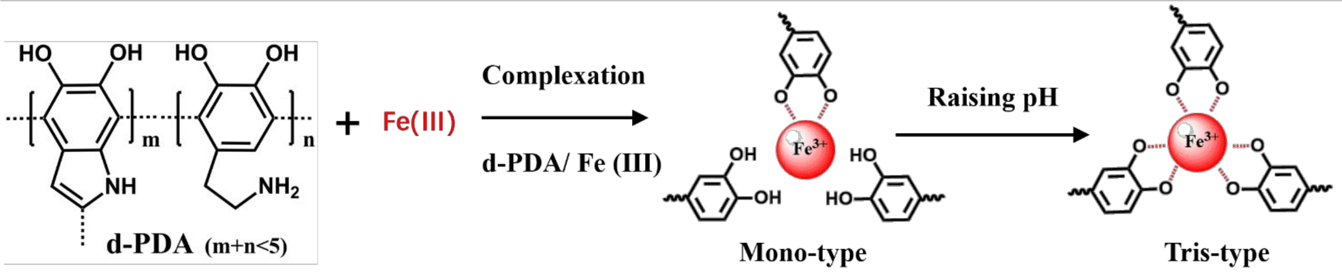

Figure S3. Proposed pH-dependent d-PDA/Fe(III) complexation state.

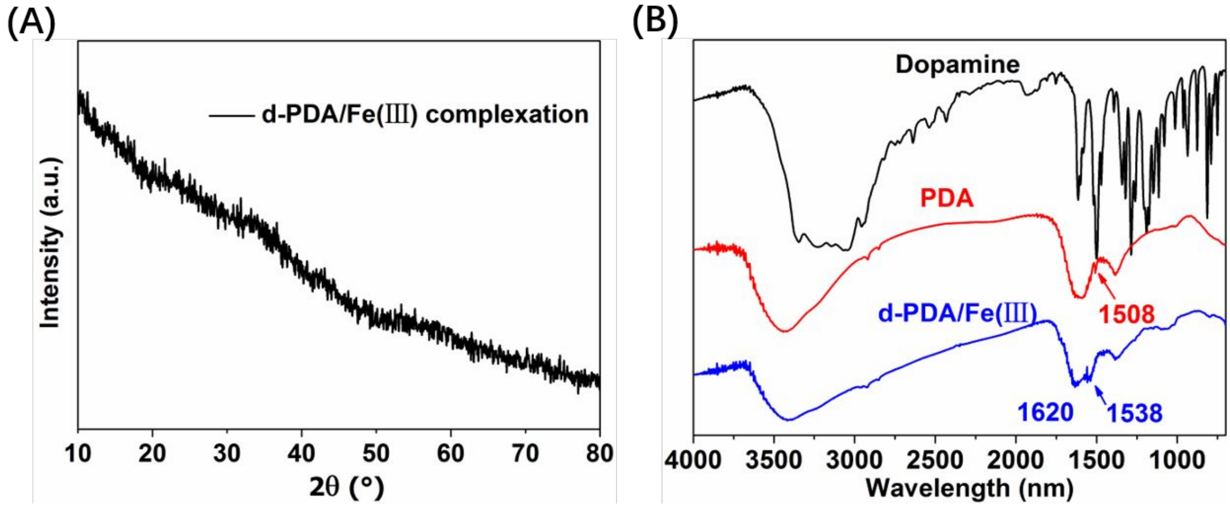

Figure S4. (A) XRD analysis of d-PDA/Fe(Ⅲ) complex powders. (B) FTIR spectra of DA, PDA, and d-PDA/Fe(Ⅲ) powders.

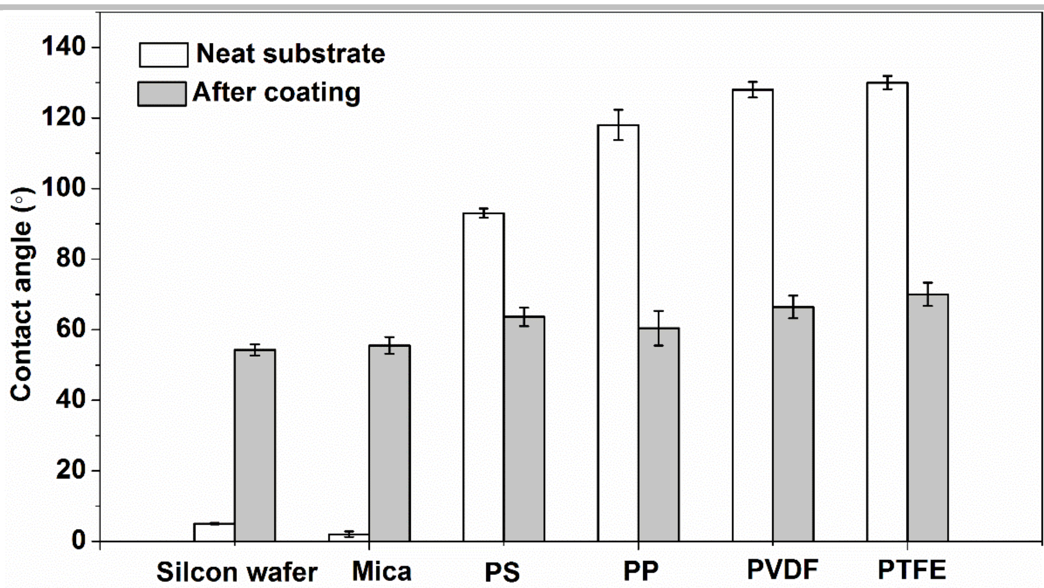

Figure S5. the contact angle of various substrates before and after coating modification, respectively.

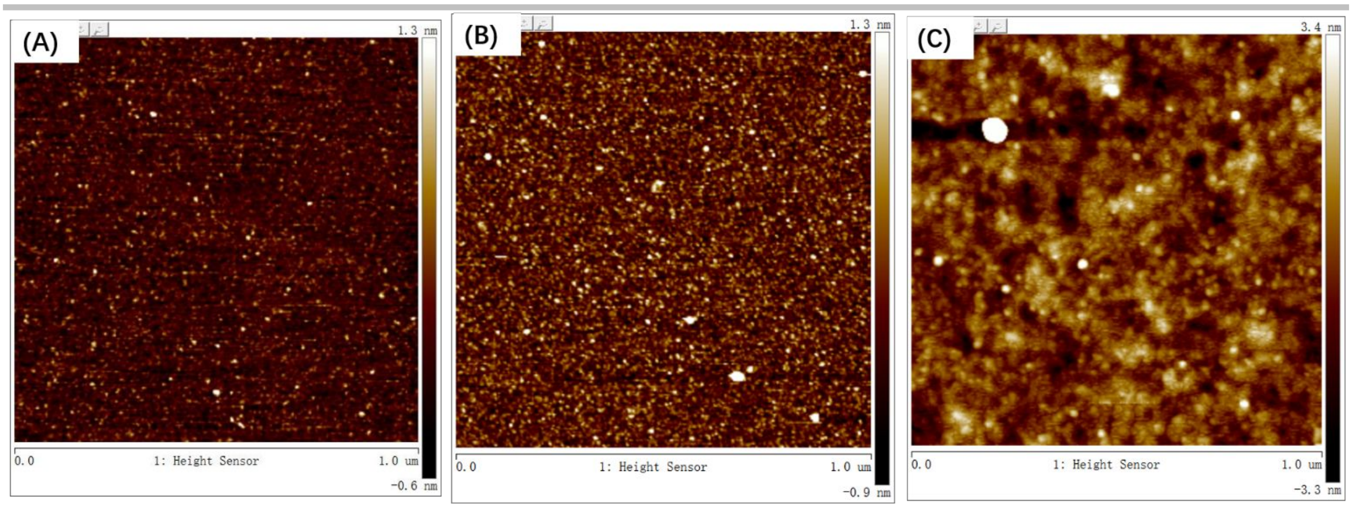

Figure S6. AFM images of mica surfaces with 1 layer (A), 3 layers (B) and 10 layers (C) of d-PDA/Fe(Ⅲ) complex films, respectively. The root mean square (RMS, nm) values of each samples are 0.19 nm, 0.32 nm and 1.21 nm, respectively.

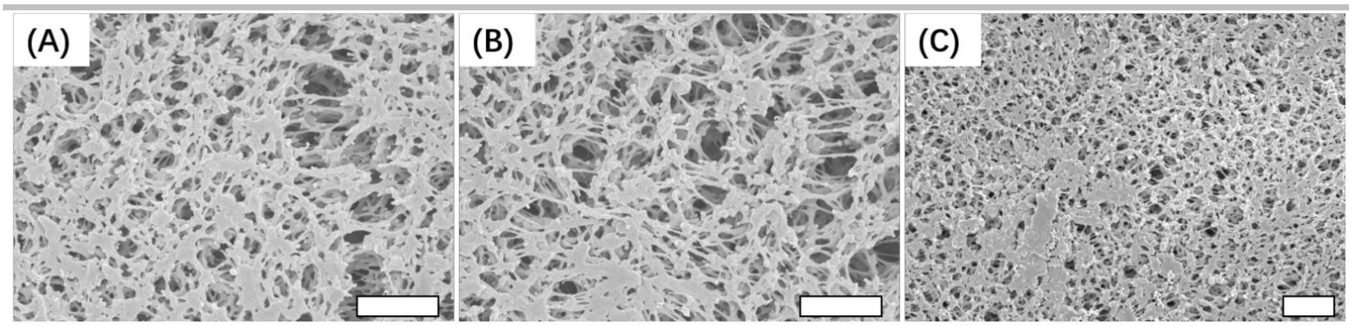

Figure S7. SEM images of PP membranes before (A) and after coating with d-PDA/Fe(Ⅲ) complex film (B), respectively. (C) PP membrane modified by self-oxidation and assembly of dopamine. All scale bar is 2 μm.

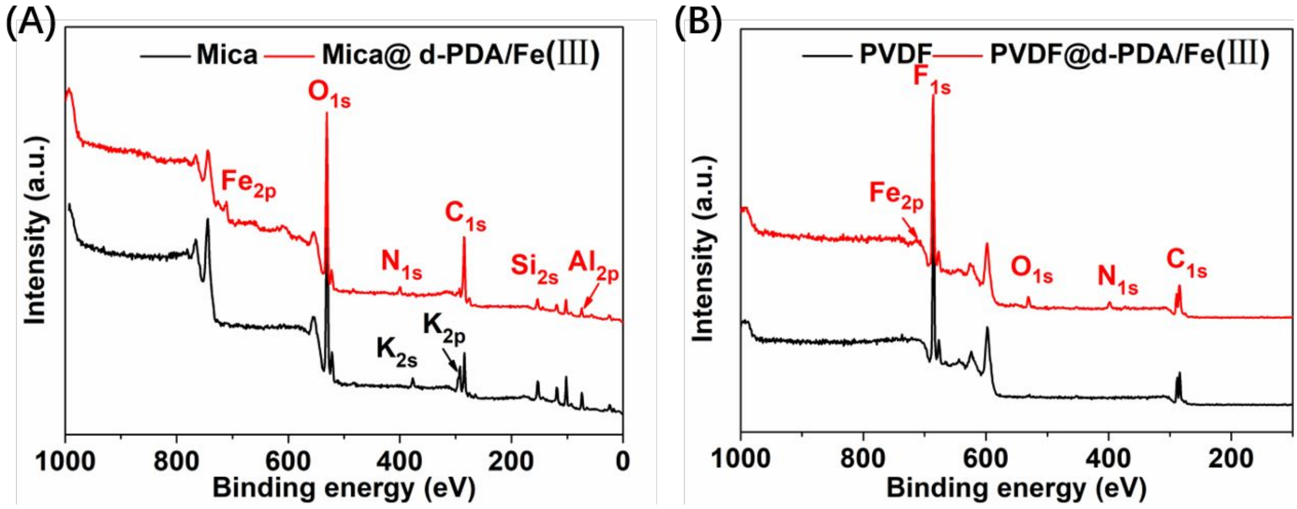

Figure S8. XPS spectra of coated and neat Mica (A) and PVDF (B) substrate, indicating the versatility of coating method on various substrates.

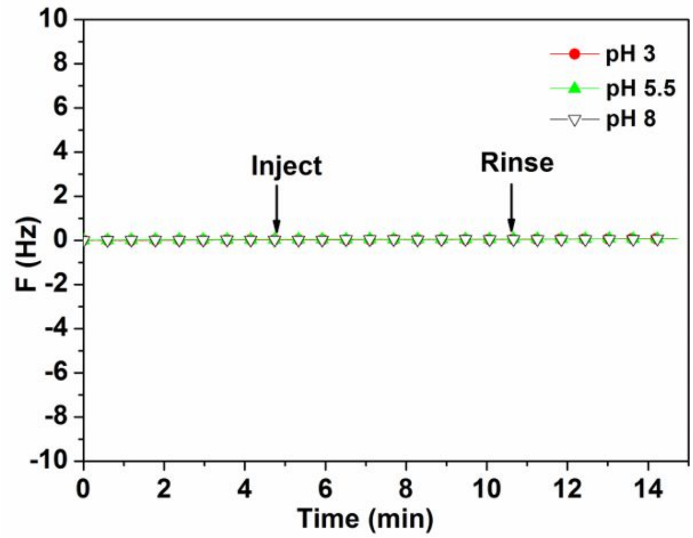

Figure S9. the frequency changes of d-PDA solution with different pH condition monitored by QCM-D.

It is possibly because the d-PDA has strong hydration interaction with the bulk water molecules and the hydration repulsion and electrostatic repulsion between d-PDA and silica substrate prevent the deposition of d-PDA on silica sensor.

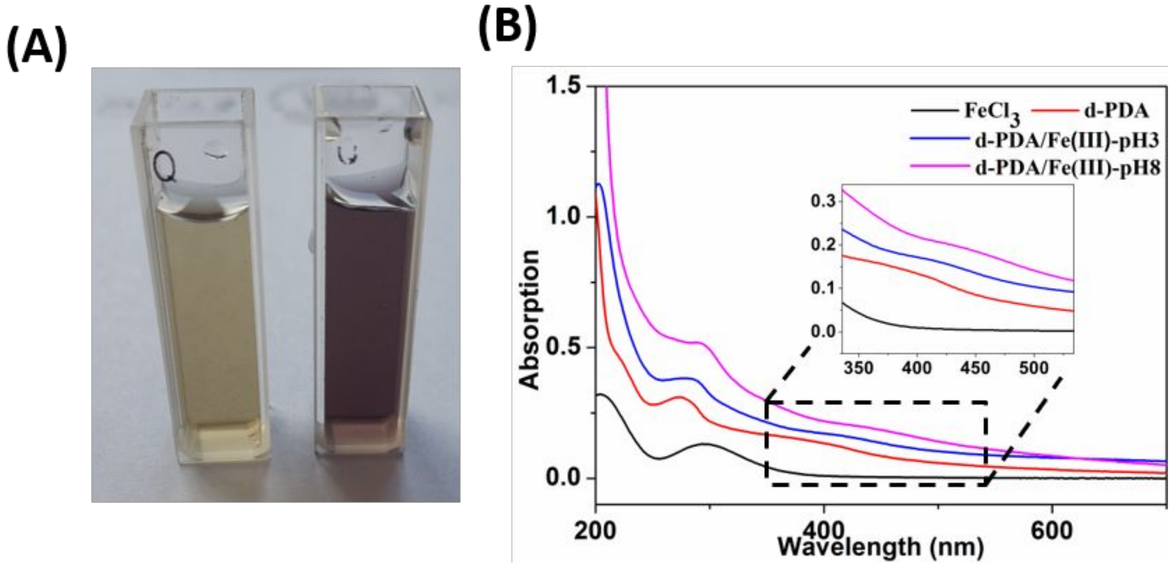

Figure S10. (A) UV-vis absorption spectra of d-PDA, and d-PDA/ Fe(Ⅲ) in solution with various pH values. The inset shows the picture of d-PDA/ Fe(Ⅲ) solution with pH =3 and pH = 8, respectively (molar ratio of d-PDA to Fe(Ⅲ) is 1:1).

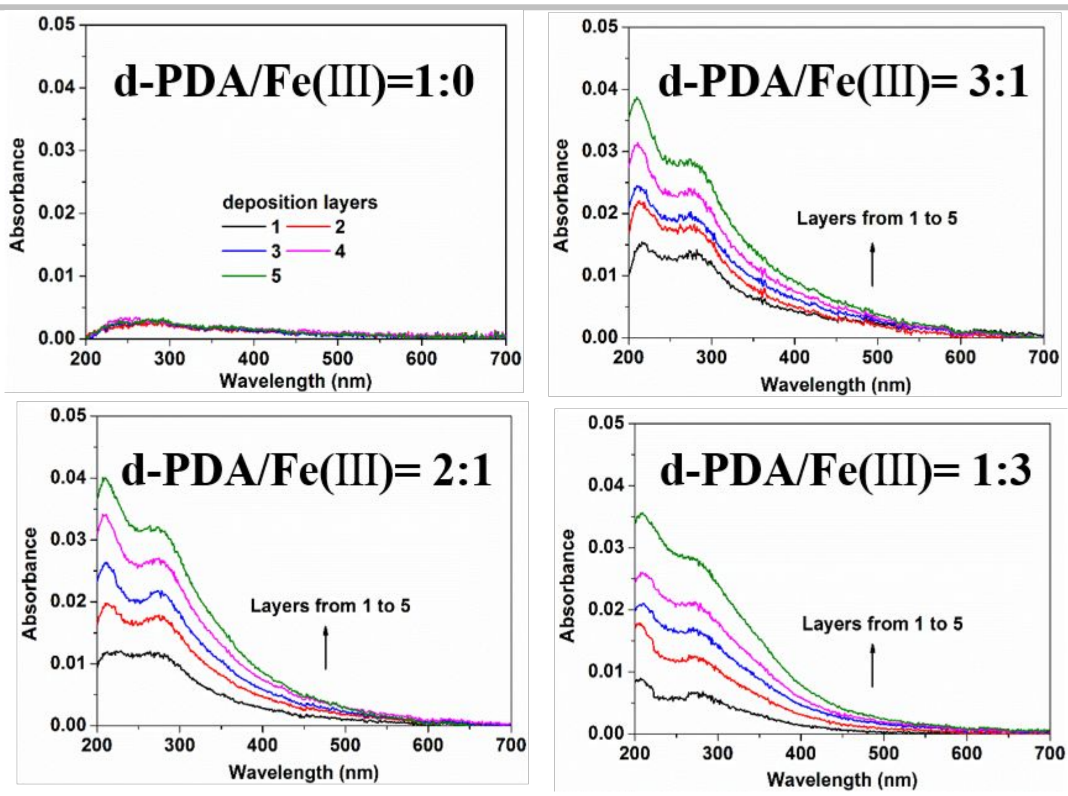

Figure S11. UV-vis spectra of complex films on quartz substrate with increasing deposition steps from 1 to 5 layers. The composition ratio of d-PDA to Fe(Ⅲ) is about 1:0, 3:1, 2:1, and 1:3, respectively.

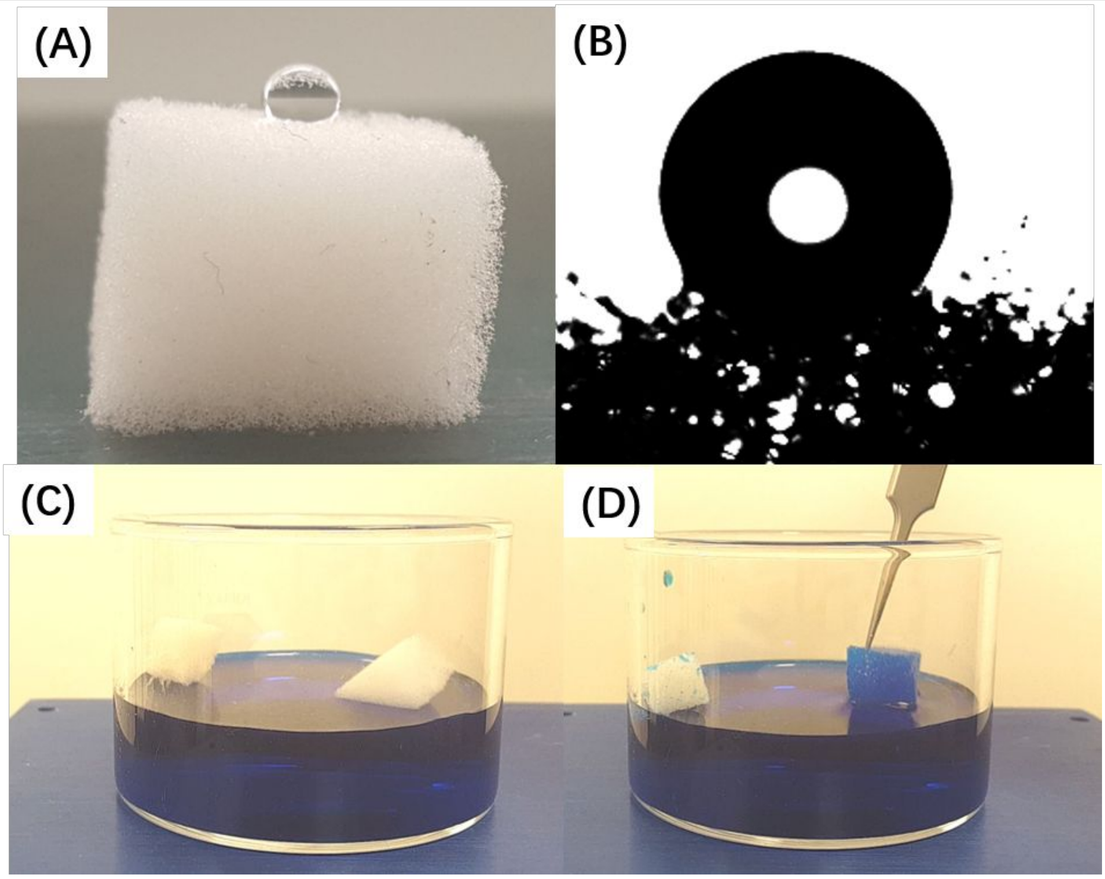

Figure S12. (A) Photo image of water droplet at alkylated d-PDA/Fe(Ⅲ) @PU substrate surface. (B) Contact angle measurement of water droplet at the surface. WCA= 135.2º (C) Modified PU sponge (left) is float at the water surface and neat PU sponge (right) is sinking when putting on the surface. (D) Neat PU sponge is totally wetted by water and the modified sponge is floating even after press into water.

After rinsing overnight, it was found that the surface wettability dramatically changed to be hydrophobic because of the successfully covalent link of long alkane chain onto surface through reaction between thiol and catechol group. Moreover, the sponge could be cut into pieces, and both pieces exhibited similar hydrophobicity like the outer layer did, indicating uniformly modification ability through this way. The 3D interconnected porous structure together with the hydrophobic alkane chain was contributed to the hydrophobicity of the sponge, where microstructure could enhance the hydrophobicity by trapping air cushion beneath the water droplet[2].

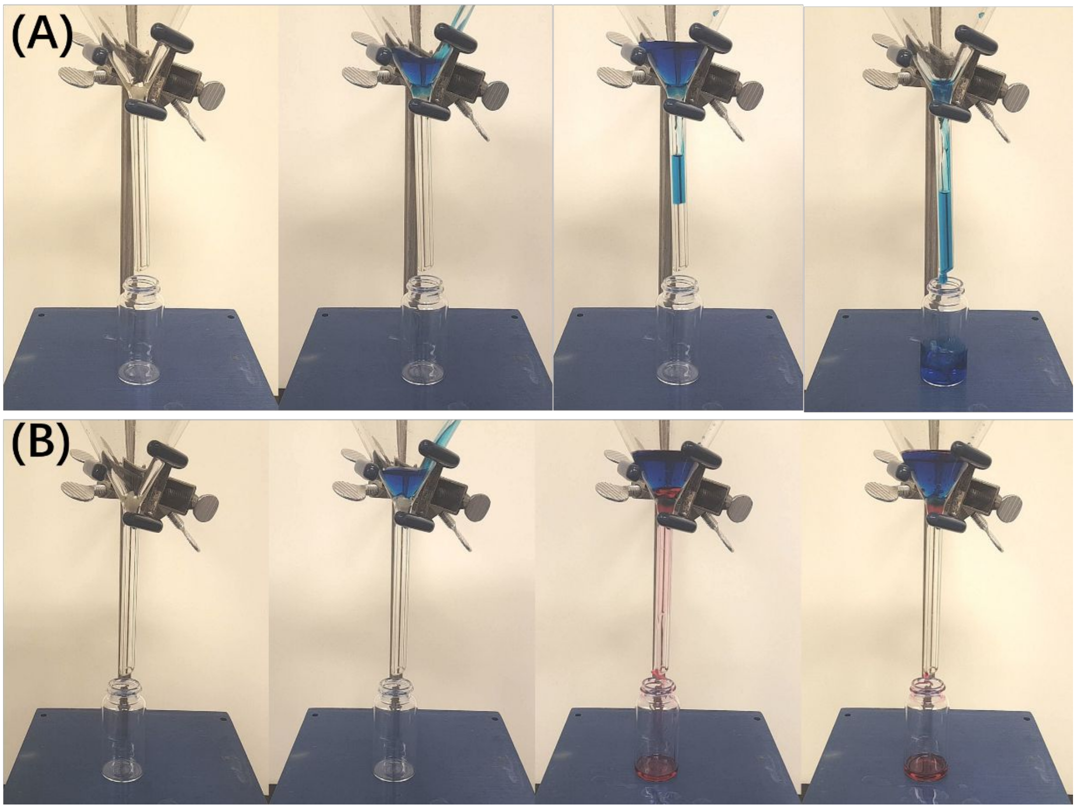

Figure S13. (A) Photo images of water (dyed with methylene blue) flow through neat PU sponge and the sponge is completely wetted. (B) Oil-water separation by alkylated d-PDA/Fe(Ⅲ)@ PU sponge, where chloroform is dyed with oil red O and water is dyed with methylene blue.

Table S1. Chemical compositions of d-PDA/Fe(III) coating on mica substrate from XPS analysis.

Element (mol %)	C	O	Al	Si	K	N	Fe	N/Fe
mica	19.1	53.2	10.6	13.0	4.1	/	/	/
mica@d-PDA/Fe(Ⅲ)	42.5	38.8	6.4	7.4	/	3.5	1.4	2.5

Table S2. Chemical compositions of d-PDA/Fe(III) coating on PVDF substrate from XPS analysis.

Element (mol %)	C	O	F	N	Fe	N/Fe
PVDF	47.9	1.0	51.1	/	/	/
PVDF@d-PDA/Fe(Ⅲ)	50.8	6.9	40.3	1.4	0.6	2.4

References

1. Chen, C. T.; Martin-Martinez, F. J.; Jung, G. S.; Buehler, M. J. Polydopamine and eumelanin molecular structures investigated with ab initio calculations. *Chem. Sci.* **2017,** *8* (2), 1631-1641.

2. Wang, S.; Liu, K.; Yao, X.; Jiang, L. Bioinspired Surfaces with Superwettability: New Insight on Theory, Design, and Applications. *Chem. Rev.* **2015,** *115* (16), 8230-93.