# Fluorine-free Superhydrophobic/Hydrophobic Polybenzoxazine/TiO $\mathbf{2}_{2}$ Films with 

Excellent Thermal Stability and Reversible Wettability

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## Supplementary information

## Chemical structure of MP-aptms and poly(MP-aptms)

To confirm the structure of MP-aptms and poly(MP-aptms), a qualitative infrared analysis was undertaken as shown in Figure S1. The absorption peak corresponding to asymmetric stretching vibration of C-O-C at $1227 \mathrm{~cm}^{-1}$ and bending vibration of $\mathrm{C}-\mathrm{H}$ out plane at $935 \mathrm{~cm}^{-1}$ disappears after curing, ${ }^{1}$ which confirm the opening of the oxazine ring and the occurrence of polymerization reaction. In the meantime, the disappearance of asymmetric stretching vibration of Si-O-C at $1086 \mathrm{~cm}^{-1}$ and the emergence of a peak at $1113 \mathrm{~cm}^{-1}$ reveal the formation of Si-O-Si. Hence, the ringopening reaction of MP-aptms and the cross-linkage of Si-O-Si occurred simultaneously by curing at $200^{\circ} \mathrm{C}$ for 1 h (Scheme S1). Cross-linking structures were formed in poly(MP-aptms).


Scheme S1 Synthesis of a) MP-aptms and b) poly(MP-aptms)


Figure S1 FTIR spectra of a) MP-aptms and b) poly(MP-aptms)


Figure S2 Photograph of water droplet on pristine glass substrated, PBZ film and $\mathrm{PBZ} / \mathrm{TiO}_{\mathbf{2}}$
film. Water droplet was dyed with methylene blue.


Figure S3 Water CA (left) and SA (right) image of PBZT11 surface. The rolling direction of water droplet on PBZT11 surface is indicated by red arrow
a)

b)

c)



Figure S4 Water CA images of a) PBZ, b) PBZT5 and c) PBZT40. The left, middle and right images are photographed when the base was tilted for $0^{\circ}, \mathbf{9 0}^{\circ}$ and $180^{\circ}$ respectively


Figure S5 Variations in water CA of PBZT11 after sandpaper abrasion test

## Reference

1 J. Liu, X. Lu, Z. Xin and C. Zhou, Langmuir, 2013, 29, 411-416.

