

## Supporting Information

### Photoresponsive Superhydrophobic Surfaces from One-Pot Solution

#### Spin Coating Mediated by Polydopamine

Jing Zhang, <sup>a,b</sup> Weidong Zhang, <sup>\*a</sup> Nianchen Zhou, <sup>b</sup> Yuyan Weng <sup>a</sup> and Zhijun Hu <sup>\*a</sup>

<sup>a</sup> Center for Soft Condensed Matter Physics and Interdisciplinary Research & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China

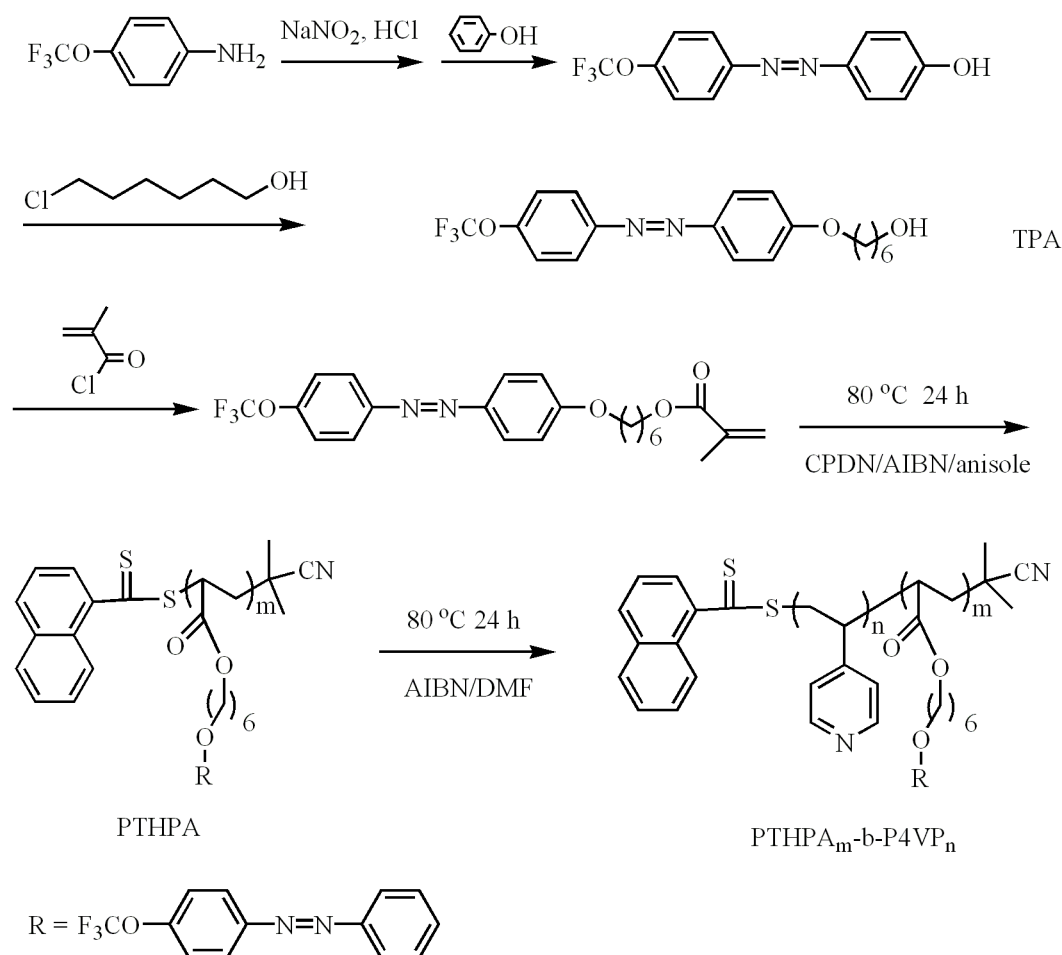
<sup>b</sup> Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Email: zhijun.hu@suda.edu.cn (Z.H.); zhangweidong@suda.edu.cn (W. Z.)

## Experimental Section

### Synthetic routes of monomers and polymers containing azobenzene moieties:

The synthetic routes of the monomers and polymers are shown in Scheme S1.



**Scheme S1.** Synthetic routes for preparation of TPA, PTHPA and PTHPA<sub>m</sub>-b-P4VP<sub>n</sub>

**The synthesis of azobenzene-containing monomers:** The 4-trifluoromethoxy[4-(6-hydroxyhexoxy)phenyl] azobenzene (TPA) was synthesized by the coupling reaction of 4-hydroxy-4-trifluoromethoxy azobenzene and 6-chlorohexanol. The 4-trifluoromethoxyphenyl[4-hexoxyl(2-methylacrylate)phenyl] azobenzene (THPA) was obtained by reacting of TPA with methacryloyl chloride. The crude product was purified by recrystallization from hexane. <sup>1</sup>H NMR (400 M Hz, CDCl<sub>3</sub>, δ): 7.97 - 7.84 (m, 4H, Ar H), 7.33 (d, *J* = 8.2 Hz, 2H; Ar H), 7.00 (d, *J* = 9.0 Hz, 2H; Ar H),

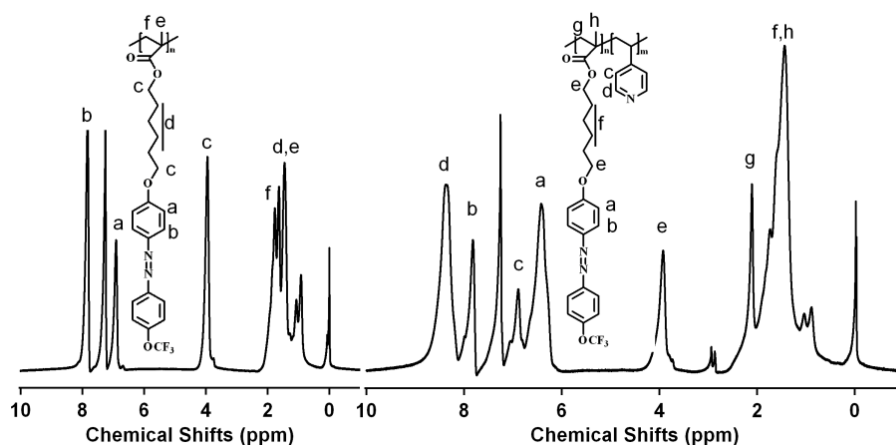
6.10 (s, 1H, C = CH<sub>2</sub>), 5.55 (s, 1H, C = CH<sub>2</sub>), 4.17 (t, *J* = 6.6 Hz, 2H; OCH<sub>2</sub>), 4.05 (t, *J* = 6.4 Hz, 2H; OCH<sub>2</sub>), 1.95 (s, 3H, CH<sub>3</sub>), 1.89 - 1.81 (m, 2H, CH<sub>2</sub>), 1.73 (dt, *J* = 13.3, 6.6 Hz, 2H; CH<sub>2</sub>), 1.62 - 1.39 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>).

**The synthesis of azobenzene-containing homopolymer:** 1500 mg (3.7 mmol) of monomer THPA, 3 mg (0.018 mmol) of azobisisobutyronitrile (AIBN), 20.1 mg (0.074 mmol) of 2-cyanoprop-2-yl dithionaphthalate (CPDN) and 4.8 ml anisole were introduced into a 5 ml dry glass tube. After purging with nitrogen for 15 min to remove the oxygen, the glass tube was sealed and placed in an oil bath at 80 °C to initiate the polymerization. At the end of the reaction (24 h), the glass tube was cooled in ice water. The contents were diluted with tetrahydrofuran (THF) and precipitated into a large amount of methanol. The obtained polymer, poly (4-trifluoromethoxyphenyl[4-hexoxyl(2-methylacrylate)phenyl] azobenzene) (PThPA), was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The PThPA yield was about 1.13 g, and the conversion of monomer was about 75%.

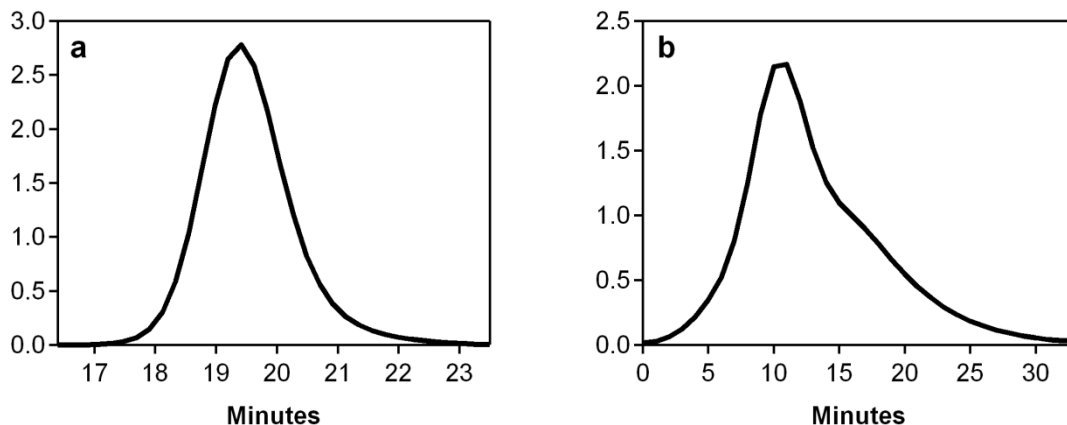
**The synthesis of azobenzene-containing diblock copolymer:** The procedures used for the block copolymerization poly(4-trifluoromethoxyphenyl[4-hexoxyl(2-methylacrylate)phenyl] azobenzene-*b*-4-vinylpyridine) (PThPA<sub>m</sub>-*b*-P4VP<sub>n</sub>) were similar to those used for the RAFT polymerization of PThPA. 1.15 ml (10.7 mmol) of 4-vinylpyridine, 819.6 mg (0.053 mmol) of PThPA, 2.9 mg (0.018 mmol) of AIBN and 1.7 ml DMF were introduced into a 5 ml dry glass tube. The light yellow homogeneous solution was purged with nitrogen for 15 min to remove the oxygen. Then, the glass tube was sealed and placed in an oil bath at 70 °C to initiate the polymerization. At the end of the reaction (24 h), the glass tube was cooled in ice water. The contents were diluted with THF, and precipitated into a large amount of petroleum ether. The polymer, PThPA<sub>m</sub>-*b*-P4VP<sub>n</sub>, was dried under reduced pressure at room temperature for at least 23 h until a constant weight was obtained. The PThPA<sub>m</sub>-*b*-P4VP<sub>n</sub> yield was about 1.38 g, and the conversion of monomer was about 75%.

**Characterization:**  $^1\text{H}$  NMR spectra were recorded by using a UNITY INOVA 400 (400.13 MHz for  $^1\text{H}$ ) nuclear magnetic resonance instrument with deuterated chloroform ( $\text{CDCl}_3$ ) or deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ) as the solvent, tetramethylsilane (TMS) as the internal standard. Chemical shifts were expressed in parts per million (ppm). The number-average molecular weight ( $M_n$ ) and polydispersity index value (PDI) of polymers were measured by means of gel permeation chromatography (GPC; waters1515, column; PLgel 10  $\mu\text{m}$  MIXED-B). The GPC measurements were carried out with THF and DMF as solvent at a rate of 1 mL/min at 30°C and the GPC result was calibrated with poly(methyl methacrylate) (PMMA) as standards. Thermogravimetric analysis (TGA) was obtained from a TGA-7 thermal gravimetry instrument.

The  $^1\text{H}$  NMR spectra of PTHPA and  $\text{PTHPA}_m\text{-b-P4VP}_n$  were shown in Figure S1. The GPC elution curves of PTHPA and  $\text{PTHPA}_m\text{-b-P4VP}_n$  given in Figure S2 exhibited narrow and symmetric shapes with relatively narrow molecular weight distributions ( $M_w/M_n$ ). These results confirm that the well-controlled PTHPA and  $\text{PTHPA}_m\text{-b-P4VP}_n$  were successfully prepared by RAFT polymerization.

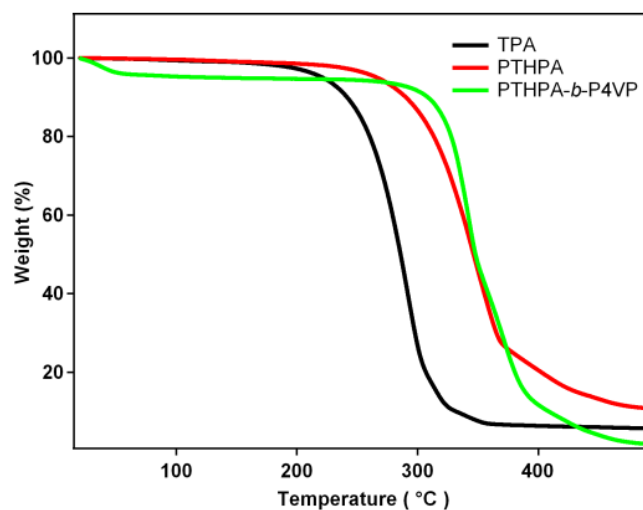


**Figure S1.**  $^1\text{H}$  NMR spectra of the polymers PTHPA and  $\text{PTHPA}_m\text{-b-P4VP}_n$  ( $m=37$ ,  $n=125$ ).



**Figure S2.** GPC curves of (a) PTHPA ( $M_n=15000$  g/mol,  $M_w/M_n = 1.16$ ) and (b) PTHPA<sub>m</sub>-*b*-P4VP<sub>n</sub> ( $M_n=28000$  g/mol,  $M_w/M_n= 1.32$ ).

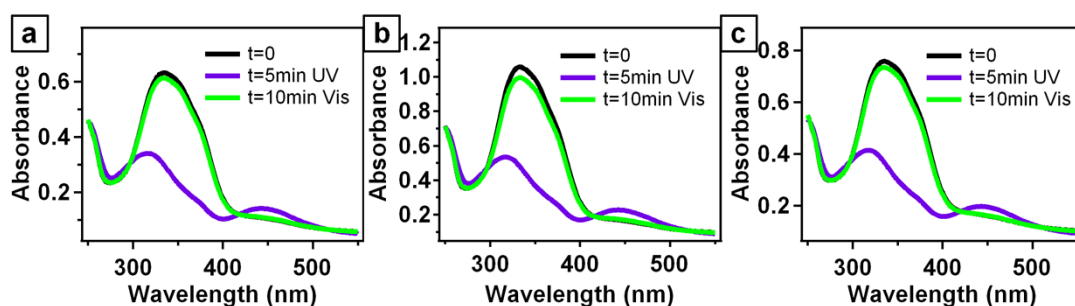
The TGA data from TPA, PTHPA and PTHPA<sub>m</sub>-*b*-P4VP<sub>n</sub> were also displayed in Figure S3. The decomposition of TPA occurs at a lower temperature than the decomposition of PTHPA and PTHPA<sub>m</sub>-*b*-P4VP<sub>n</sub>, indicating that the stability of the polymers is much higher than the small molecules of TPA.



**Figure S3.** Thermogravimetric analysis of samples TPA, PTHPA and PTHPA<sub>m</sub>-*b*-P4VP<sub>n</sub>

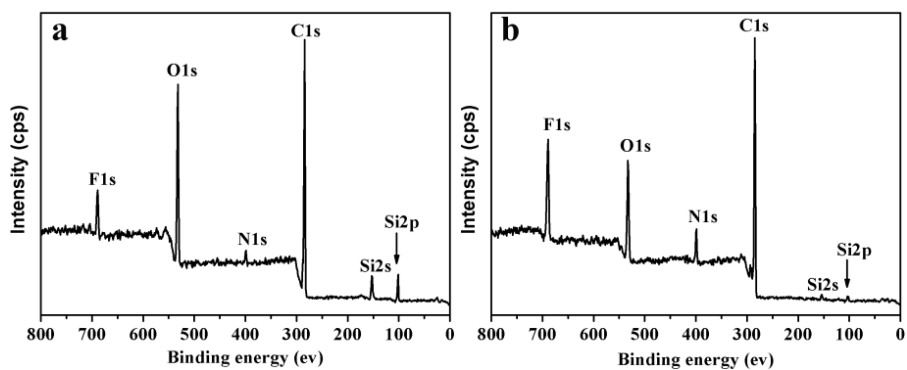
The UV/vis spectra of silica/PD/TPA film were measured with a UV-VIS-NIR spectrophotometer (UV-3600, SHIMADZU Co.) (Figure S4a). The change of the UV-

Vis absorption spectra was caused by trans-cis isomerization of TPA. Two absorption peaks (centered at 340 and 450 nm) were due to the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition bands of trans-azobenzene respectively. Under UV irradiation, trans isomerized to cis. And the film attained to a photostationary state of the cis isomer predominates when it exceeded a UV irradiation period (5 min). After visible irradiation for 10 min, the cis recovered to the trans. The change of the UV-Vis absorption spectra of silica/PD/PTHPA film and silica/PD/PTHPA<sub>m</sub>-b-P4VP<sub>n</sub> film upon UV and visible irradiation were also investigated (Figure S4b and S4c).

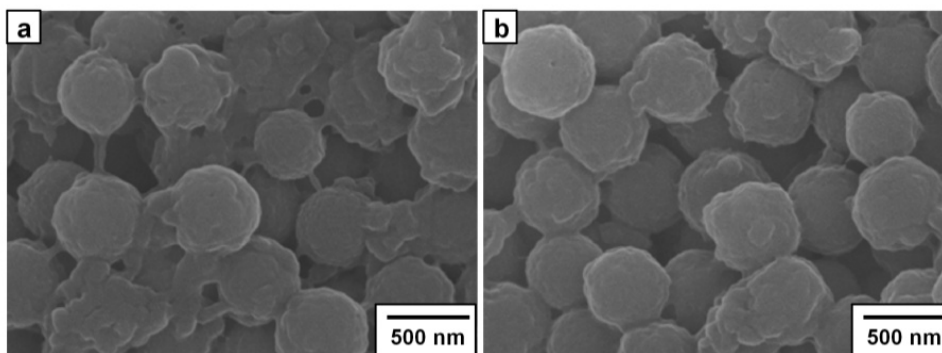


**Figure S4.** UV-Vis absorption spectra of a) silica/PD/TPA film b) silica/PD/PTHPA film c) silica/PD/PTHPA<sub>m</sub>-b-P4VP<sub>n</sub> film

The successful immobilization of functional materials onto the PD coated silica particles is not limited to azobenzene derivative TPA with low molecular weight. As shown in Figure S5a and S5b, new F 1s peaks all appeared in the spectrum, indicating that the fluorinated azobenzene polymers PTHPA and PTHPA<sub>m</sub>-b-P4VP<sub>n</sub> were adhered on the rough surface of silica/PD particles. Moreover, rough surfaces (Figure S6) all could be obtained. By mixture silica/PD and smart materials, the smart complex particles can easily formed. This strategy has an incredible benefit for fabricating complex particles.

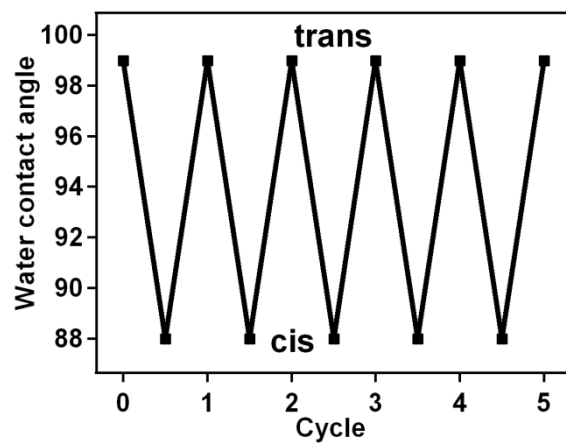


**Figure S5.** XPS spectrums of a) silica/PD/PTHPA b) silica/PD/PTHPA<sub>m</sub>-b-P4VP<sub>n</sub>



**Figure S6.** SEM photographs of a) silica/PD/PTHPA particles and b) silica/PD/PTHPA<sub>m</sub>-b-P4VP<sub>n</sub> particles.

**Preparation of samples on the PD-modified silicon wafer:** Firstly, silica wafers are dispersed in dopamine solution at pH of 8.5. After 24 hours, PD coated silicon wafers (silicon/PD) are obtained due to pH-induced, oxidative polymerization of dopamine-hydrochloride. Secondly, the fluorinated azobenzene derivative TPA is immobilized onto the surface of PD-modified silicon wafer by dispersing the silica wafer in the solution. Then the water CAs of the surface of the samples were tested under UV/visible irradiation (Figure S8).



**Figure S8.** Reversible wettability transitions of the surface of silicon/PD/TPA under alternate UV and visible light irradiation.