Electronic Supplementary Information

Saccharide-Sensitive Wettability Switching on a Polymer Surface Containing Thiourea and Phenylboronic acid Units

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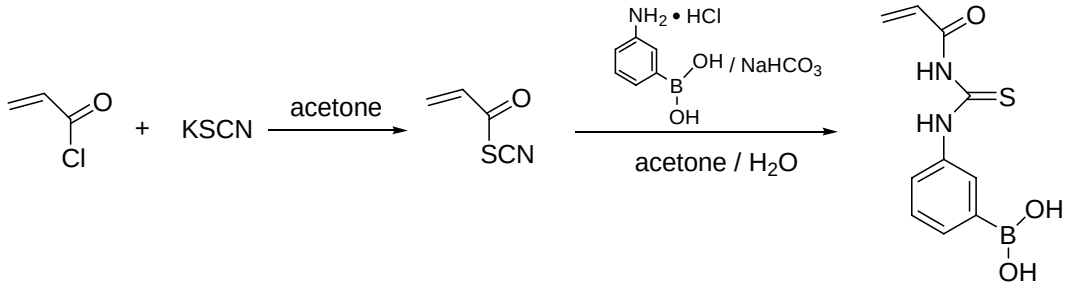
I. Materials and Methods

Chemicals: N-isopropyl acrylamide (Aldrich, Germany) was recrystallized in n-hexane for three times. Silicon wafer was purchased from Silicon Materials Corporation (Germany). The 3-arylamido phenylboronic acid (PBA) was synthesized according to the literature.[1] 3-aminophenylboronic acid hydrochloride (Sigma, Germany), aniline, acetone, nitric acid, methanol, DMF, sodium hydroxide, bromoisobutyryl bromide (Alfa, Germany), *N,N,N',N',N"*-Pentamethyl- diethylenetriamine (Aldrich, Germany) and 3-aminopropyl trimethoxysilane (Fluka, Switzerland) were used as received. CuBr was recrystallized before being used. Toluene, dichloromethane were dried by molecular sieves for 24 hours before being used. Double distilled water (5.5 MΩ·cm, MilliQ system) was used. Various saccharides used in the detection were purchased from Alfa.

Synthesis of 3-(acryloylthioureido) phenylboronic acid

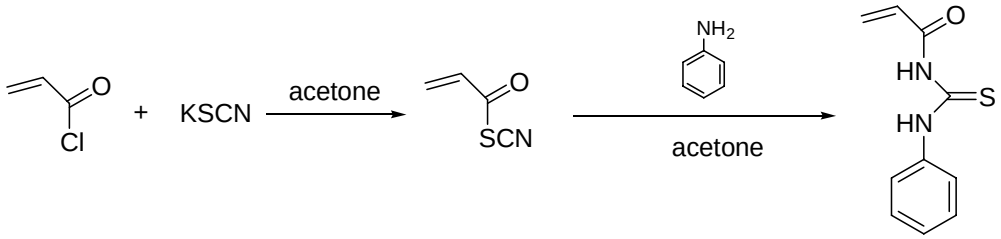


Scheme S1 The synthesis of 3-(acryloylthioureido) phenylboronic acid.

Acryloyl chloride (0.678 g, 7.5 mmol) was added into a solution of KSCN (0.727 g, 7.5 mmol) in 15 mL dry acetone, and the reaction mixture was stirred at ambient temperature overnight. After filtration, the yellow filtrate was collected and stored in cuvette for the next step directly.

$NaHCO_3$ (0.484 g, 5.77 mmol) was added to a solution of 3-aminophenyl boronic acid hydrochloric acid (1.0 g, 5.77 mmol) in 40 mL acetone and H_2O (v/v 1:1), the mixture was stirred for 10 min, then the filtrate made above was added stepwise to the mixture and continue to stir for 24 hours. The mixture was extracted with acetate ethylate for three times. The organic layer was collected and dried over anhydrous Na_2SO_4. After filtration and evaporation of solvent, the crude product was purified on a silica gel column, with elution with CH_2Cl_2/MeOH (15:1), to give target compound as white powder (0.79g, yield:54.8%). ^{1}H NMR (300MHz, d_6-DMSO): 5.73 (d, *J*=15.3 Hz, 1H, =CH), 6.21 (d, *J*=22.5 Hz, 1H, =CH), 6.45 (m, 1H, =CH), 6.98 (s, 1H, Ph-H), 7.30 (m, 1H, Ph-H), 7.50 (m, 1H, Ph-H), 7.79 (m, 1H, Ph-H), 8.05 (s, 2H, B-OH), 10.08 (s, 1H, CN*H*CS), 10.97 (s, 1H, ArN*H*CS); ^{13}C NMR (300MHz, d_6-DMSO): 121.3, 125.0, 125.3, 126.6, 127.8, 129.1, 131.9, 138.2, 147.2, 162.9; Quattro-LC MS: m/z calcd for $C_{10}H_{11}BN_2O_3S$: 250.058; found: 249.1.

Synthesis of acryloyl phenylthiourea



Scheme S2 The synthesis of acryloyl phenylthiourea

Similar method was used to synthesize acryloyl phenylthiourea. The crude product was purified on a silica gel column, with elution with CH_2Cl_2/MeOH (150:1), to give target compound as semi-oil powder (yield: 47.4%).^{1}H NMR (300MHz, $CDCl_3$): 6.00 (d, *J*=25.5Hz, 1H, =CH), 6.27 (d, *J*=27Hz, 1H, =CH), 6.61 (m, 1H, =CH), 7.19 (m, 1H, Ph-H), 7.47 (m, 1H, Ph-H), 7.75 (m, 1H, Ph-H), 9.35 (s, 1H, CN*H*CS), 12.54 (s, 1H, ArN*H*CS); ^{13}C NMR (300MHz, $CDCl_3$): 124.9, 126.3, 129.1, 129.2, 132.1, 138.1, 169.8, 183.5; MADLI: m/z calcd for $C_{10}H_{10}N_2OS$: 206.051; found: 229.1 ($M+Na^+$).

Synthesis of copolymer films on silicon substrate

A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 8 minutes and subsequently in HNO_3 (0.1 M) for 15 min to generate surface hydroxyl groups. After the substrate had been washed with an excess of water and dried under a flow of nitrogen, it was heated to reflux in toluene that containing 5 wt% aminopropyl trimethoxysiliane (ATMS) for at least 6 hours to obtain chemically bonded $-NH_2$ groups on the surface. The surface was rinsed with toluene and dichloromethane to remove remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry dichloromethane that contained pyridine (2% v/v). The polymerization initiator bromoisobutyryl bromide was added dropwise into the solvent containing the silicon substrate at 0 ^{o}C, and the mixture was left for 1 hour at this temperature then at room temperature for 12 hours. The silicon substrate was cleaned with dichloromethane, and dried under a nitrogen flow. Polymerization of the ATPBA-*co*-PNIPAAm film was achieved by immersing the silicon substrate with the initiator grafted on the surface in a degassed solution of NIPAAm (0.864 g) and ATPBA (0.347 g) (15 mol % ATPBA against NIPAAm.) in a mixture of H_2O (5 mL), MeOH (5 mL) and DMF (0.5 mL) containing CuBr (0.032 g, 0.23 mmol) and pentamethyl diethylene triamine (PMDETA, 0.16 mL) for 5 hours for the substrates, at 60 ^{o}C.

The similar protocols were used in the preparation of PBA-*co*-PNIPAAm) and TH-*co*-PNIPAAm) thin films.

Fabrication of the structured silicon substrate

The silicon wafer was used directly as the smooth substrate. The structured silicon substrate was fabricated by the combination of the photolithography and inductively coupling plasma (ICP) deep etching technique, and a chemical etching process. The photolithography and ICP technique were used to obtain the patterned silicon micropillar structure[2] on silicon wafer, and the chemical etching process, as described in detail in the literature,[3] was used to create further aligned nanofibrous structure on each micropillar.

Contact angle measurement

The static CAs were measured by a Contact Angle Measurement System G2 instrument (Krüss, Germany) at ambient atmosphere and a constant temperature of 20 ^{o}C. For the cycling experiment, a cycle includes the alternate measurement of CA after the sample was immersed in sugar solution of 5×10^{-2} M for 15 minutes and pure water for 5 minutes, respectively. All the measurements were made after the sample was dried by flow N_2 gas.

AFM study

The AFM investigation was conducted on flat silicon substrate (with polymer film on it) using a Nanoscope IIIa instrument (DI, USA) in the tapping mode.

II. Time dependence of static CA measurement on measuring time.

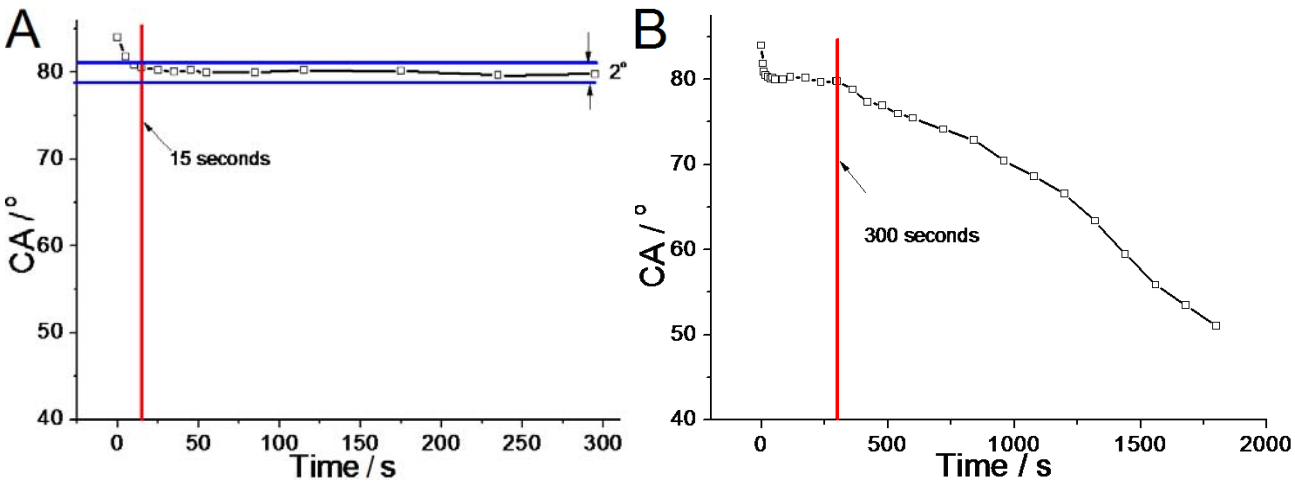


Figure S1. Time dependence of static CA measurement. (A) 0-300 seconds range. It shows that the CA value is constant (CA change is less than 2°) in the range of 10s – 300 s measuring time. (B) 1-1800 seconds range. The significant decrease of CA value is observed after 300 seconds. It is due to the evaporation of the water drop. Since our measurement is usually made in the time range of 15-20 seconds after the water drop is put onto the surface, this method is much reliable.

III. Supplementary information for the water CA measurement on different copolymer films.

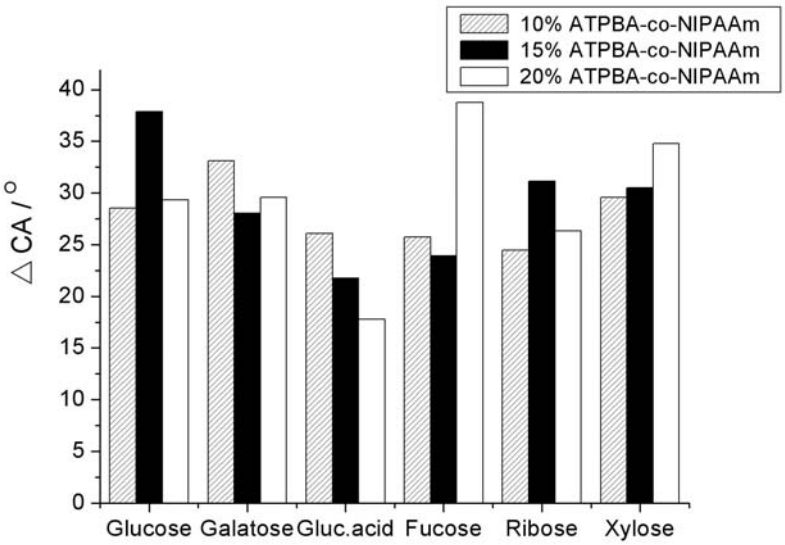


Figure S2 Water CA change of different mole-ratio ATPBA-*co*-NIPAAm film before and after being immersed in different sugar solutions (5 x 10^{-2} mol/L).

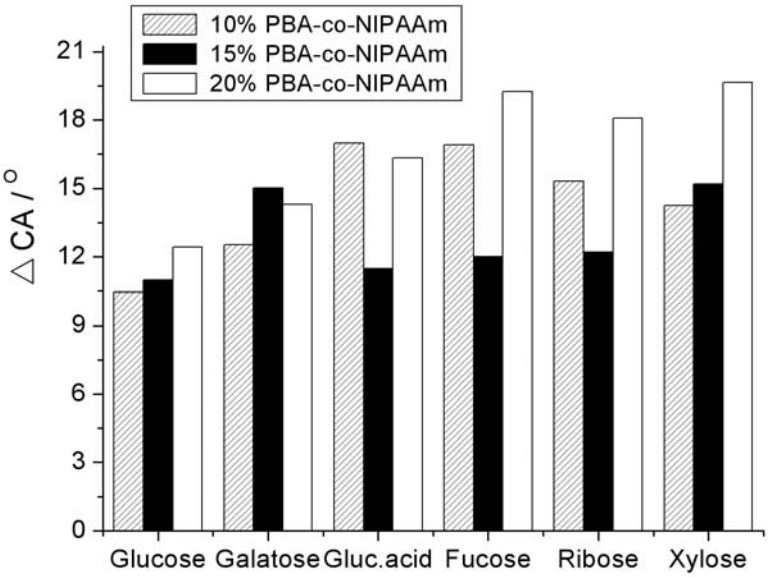


Figure S3 Water CA change of different mole-ratio PBA-*co*-NIPAAm film before and after being immersed in different sugar solutions (5 x 10^{-2} mol/L).

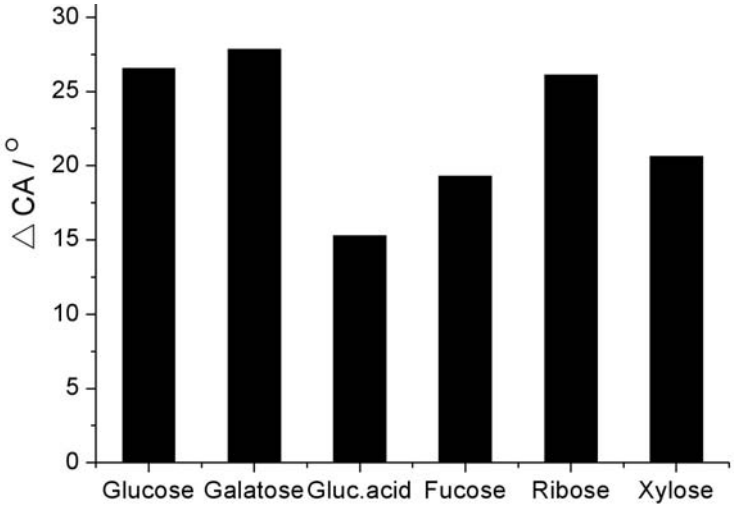


Figure S3 Water CA change of TH-*co*-NIPAAm film before and after being immersed in different sugar solutions (5 x 10^{-2} mol/L).

III. UV-vis titration experiment for the interaction between sugar and monomers of ATPBA and acryloyl phenylthiourea (ART)

Considering the solubility of monomer APT and D-glucose, we chose DMSO as the solvent to process the UV-vis titration experiment to investigate their interaction, clear change in the UV-vis spectra can be observed, in which the intensity of the absorption peaks decreases regularly with the increase of sugar content, as shown in the Fig 3a in the text. Because D-glucose has no absorption in the UV-vis spectra, the change in the spectra could only be attributed to the interaction between APT and D-glucose, while the association constant could be obtained by a non-linear least-squares analysis of *A* versus C_H and C_G (equation 1). According to calculation, we found the monomer and D-glucose could form 1:1 complex, and the association constant (K_{ass}) was 747.8 ± 68.5 M^{-1}. In this system, hydrogen

bonding interaction between thiourea and hydroxyl of glucose plays the critical role in the change of spectra, which has been described by many related references.[4]

Similarly, we use UV-titration to investigate the interaction between monomer ATPBA and D-glucose in DMSO as shown in the Figure 3b in the text. The association constant was 1058.5 ± 82.7 M^{-1}, which indicate ATPBA has stronger hydrogen bonding ability than APT.

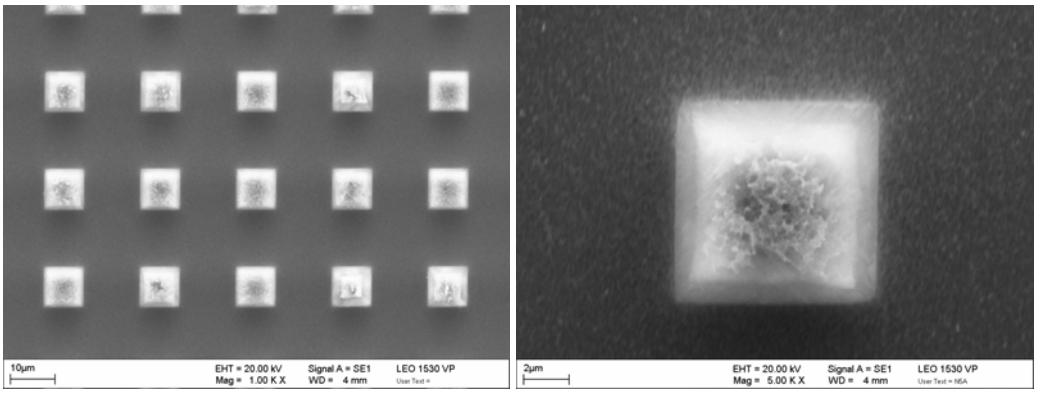
The same method was also used to determine the association constants of other sugars with ATPBA. As calculated, the values for galactose and glucuronic acid are 849.0 ± 64.6 M^{-1} and 764.4 ± 57.0 M^{-1}, respectively. These data are in good consistence with the responsive wettability results.

For the complex of 1:1 stoichiometry, an association constant K_{ass} can be calculated by using the following equation in Origin 7.0:[5]

$$A = A_0 + \frac{A_{lim} - A_0}{2C_0}\{C_H + C_G + 1/K_{ass} - [(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G]^{1/2}\} \quad \text{eq 1.}$$

Where A represents the absorption intensity, and C_H and C_G are the corresponding concentrations of host and anion guest.

IV. SEM images for the structured silicon substrate.



(a) (b)

Figure S4 Typical SEM image of the rough silicon substrate. (a) Large scale image, in which well-patterned micro-pillar structure can be observed. (b) Magnified image of a single pillar, in which further nanostructure can be observed.

Literatures

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2. Sun, T., Wang, G., Liu, H., Feng, L., Jiang, L., Zhu, D. *J. Am. Chem. Soc.* **125**, 14996-14997 (2003).
3. Peng, K., Wu, Y., Fang, H., Zhong, X., Xu, Y., Zhu, J. *Angew. Chem. Int. Ed.* **44**, 2737-2742 (2005).
4. (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419-4476; (b) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192-202; (c) Quinlan, E.; Matthews, S. E.; Gunnlaugsson, T. *J. Org. Chem.* **2007**, *72*, 7497-7503.
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