# Supplementary Material (ESI) for Chemical Communications

**SUPPORTING INFORMATION FOR**

# Photo-Switched Wettability on Electrostatic Self-Assembly Azobenzene Monolayer

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**□ Preparation of rough silicon substrate with well-defined structure**

Contact lithographic masks (with squarely arrayed square post of 10 μm and different spacing between two adjacent squares of 5, 10, 15, 20, 30, 40, 50 and 60 μm, respectively.) were constructed by Microelectronics R&D Center, Chinese Academy of Science. The instrument Karsuss MA6 (Germany) was used to transfer the patterns of masks onto silicon wafers by photolithography method. The deep etching process was completed by a STS ICP ASE (UK) instrument with depth of about 20 μm.

**□ Material**

Poly {2-[4-phenylazophenoxy] ethyl acrylate-co-acrylic acid} (PPAPE) was synthesized from poly(acryloyl chloride) by postfunctionalized with 2-[4-phenylazophenoxy] ethanol (PAPE).[1] The degree of functionalization of the azo chromophore was 50%.

Poly (diallyldimethylammonium chloride) (PDAC) (MW 20000-35000, 20 % solution) was purchased from Aldrich and used after dilution. PDAC was used as polycation and was diluted to a $10^{-4}$ mol/L concentration (repeat unit) with Milli-Q water. PPAPE used as polyanion and dissolved in the Milli-Q

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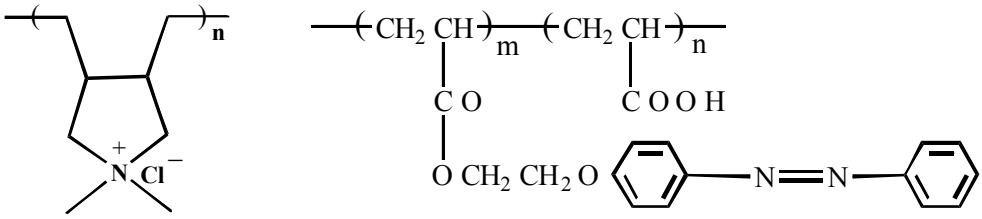
water with concentrations of $10^{-4}$ mol/L. (structural unit). A suitable amount of sodium hydrogen carbonate was added into the solution to promote the solubility of the polymers. After completely dissolving, the pH values of the solution were adjusted to be 6-7 by adding a few drops of HCl dilute solution.



**PDAC** **PPAPE**

*Scheme 1*. Chemical structure of the molecules used in the study.

**□ Preparation of azobenzene layer-by-layer films**

The clean silicon wafer and quartz wafer (45 mm × 13 mm × 1 mm) were used as adsorption substrates and were treated as follows. The wafers were immersed in a $H_2SO_4$ (98 %) : $H_2O_2$ (30 %) = 3 : 7 (volume ratio) for 2 h and taken out and washed with excess Milli-Q water for several times and then were immersed in a $H_2O$ : $H_2O_2$ (30 %): $NH_3 \cdot H_2O$ (25 % ) = 5 : 4 : 2 (volume ratio) solution for 2 h. The wafers were taken out and were washed with a thorough rinse and dried under a flow of nitrogen. A freshly treated silicon wafer and quartz wafer was alternately dipped in the PDAC solution and the PPAPE solution each for 10 mins. After each dipping, the wafer was washed with enough Milli-Q water for 2 mins.

**□ The UV, Vis light used and UV-Vis spectra**

The UV irradiating light was from a high-intensity 365 nm UV lamp equipped with 5 in. diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, L-09819-23 filter). The intensity of the lamp was 7000 and 21000 μW/cm$^2$ at distance of 15 and 2 in, respectively. The samples were placed 10-15 cm away from the lamp for 20 min. The surrounding temperature of the samples was controlled using a

cold plate set to ca. 30□. The Vis light was from a Solar Radiation Simulator equipped with a filter of 494 nm and the intensity was about 1200 μW/cm$^2$. The samples were irradiated by the visible light at room temperature for 3 h.

The UV-Vis spectra were recorded on a Perkin-Elmer Lambda Bio-40 spectrometer. From the UV-Vis spectra of multilayers (from one to ten bilayers) shown in Figure 1, it can be seen that intensity of the absorbance of the multilayers increase linearly with the number of diping, which indicates the build-up of multilayers in a Layer-by-Layer manner.[1,2] The azobenzene polyelectrolyte PPAPE exhibits its absorption maxima at about 343 nm and weak band at about 440 nm, which are related to π-π* and n-π* transition bands of the trans azobenzene, respectively. Upon UV light irradiation, the intensity of π-π* transition band at 343 nm decreases and that of n-π* transition band at 440 nm increases. Then upon Vis light irradiation, the prime spectrum of the azobenzene film recovers.

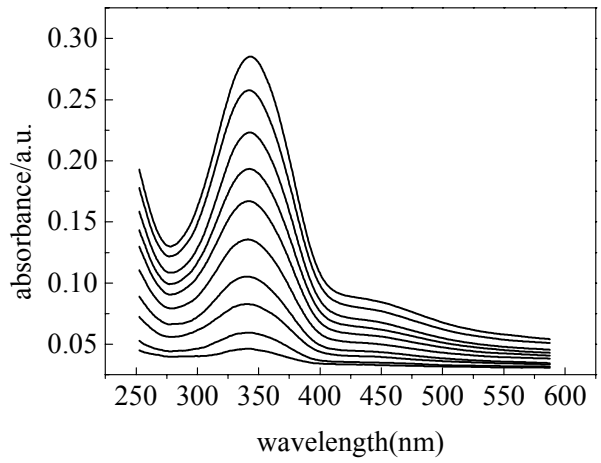



*Figure 1*. UV-Vis absorption spectra of electrostatic self-assembly azobenzene films on a quartz wafer (from bottom to top: 1 to 10 bilayers).

**□ Measurement of contact angle**

Contact angles on the electrostatic self-assembly azobenzene films were measured with an optical contact angle meter (OCA20, Dataphysics Inc) at ambient temperature. Water drop volumes were 3μl.

**References:**

(1) L F Wu, X L Tuo, H Cheng, Z Chen, X G Wang, *Macromolecules*. 2001, **34**, 8005.

(2) G J Wang, Y N He, X G Wang, L Jiang,. *Thin Solid Films*. 2004, **458**, 143.