Supporting Information

Effect of nanostructure on the surface dipole moment in photoreversibly tunable superhydrophobic surfaces

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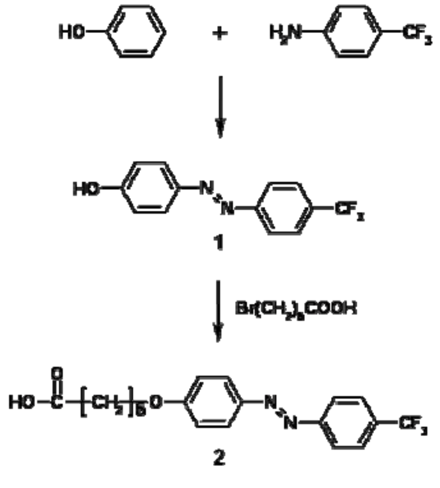
Materials: 4-(trifluoromethyl)aniline (99+%) was purchased from Acros. Phenol (99%), sodium nitrite (99%), sodium carbonate (99%), acetic acid (glacial, 99.8%), and N-ethyl-N-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) were supplied by Sigma-Aldrich and used as received. 6-bromohexanoic acid (98%), poly(allylamine hydrochloride) (PAH, mol. wt. 70,000), poly(styrene sulfonate) (PSS, mol. wt. 70,000), poly(ethylene imine) (PEI, mol. wt. 25,000), and nanosilica particles (SiO_2 nanoparticles, d ≈ 11 nm) were obtained from Aldrich. 11-amino-1-undecanethiol-hydrochloride was purchased from Dojindo Laboratories. All chemicals and solvents were used directly without further purification and were of reagent grade.

Synthesis of fluorinated azobenzene derivatives: Fluorinated azobenzene derivatives, 7-[(trifluoro methylphenylazo)phenoxy]pentanoic acid (CF3AZO), were converted from 4-(4-trifluoromethyl phenylazo)phenol, which was prepared via the diazo-coupling of 4-(trifluoromethyl)aniline with phenol by conventional procedures (**Scheme S1**).



Scheme S1. Chemical structure and synthetic procedures of the 7-[(trifluoromethylphenylazo) phenoxy]pentanoic acid (CF3AZO) used in this study.

***4-(4-trifluoromethylphenylazo)phenol* (1)**. 4-(trifluoromethyl)aniline (75 mmol) was dissolved with heating in a mixture of 21 ml concentrated sulfuric acid and 21 ml water. After cooling, the solution was diazotized by dropping a solution of 7 g sodium nitrite in 40 ml water at 0 ~ 5 °C to the acid mixture. The coupling reaction was carried out by slowly adding the diazotization solution to a solution of 7.5 g phenol, 3 g sodium hydroxide, and 47 g sodium carbonate in 270 ml water at 0 ~ 5 °C. The yellow-orange colored precipitate of 1 was removed by filtration, dried, and recrystallized from n-hexane. ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ [ppm] : 6.98 (2H, d, Ar-H), 7.76 (2H, d, Ar-H), 7.95 (4H, t, Ar-H).

***7-[(trifluoromethylphenylazo)phenoxy]pentanoic acid* (2)**. To a mixture of 4-(4-trifluoromethyl phenylazo)phenol (19.0 mmol) and powdered potassium hydroxide (42.4 mmol) in 150 ml absolute ethanol, 6-bromohexanoic acid (23.1 mmol) was added and the mixture was refluxed for 6 h. After cooling to room temperature, the inorganic salts were removed by filtration. The filtrate was acidified with 40 ml acetic acid, and the mixture was refluxed for 30 min. The solvent was removed in vacuo and 200 ml chloroform was added. The organic layer was washed three times with water and dried over sodium sulfate. Recrystallization from acetonitrile afforded orange crystals. ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ [ppm] : 1.78 (6H, m, CH_2), 2.43 (2H, t, CH_2CO), 4.07 (2H, t, CH_2O), 7.02 (2H, d, Ar-H), 7.75 (2H, d, Ar-H), 7.96 (4H, d, Ar-H).

UV/vis spectra of the azobenzene derivatives in methylene chloride solution

The UV/vis spectra of 7-[(trifluoromethylphenylazo)phenoxy]pentanoic acid (CF3AZO) in CH_2Cl_2 solution were measured with a UV-vis-NIR spectrophotometer (Cary 5000, Varian Co.) (**Figure S1**). The absorption spectrum changed considerably as a result of *trans-cis* isomerization. The absorption maximum of the CF3AZO azobenzene solution was 355 nm, with a weak band at 434 nm, which arose from due to the π-π^* and n-π^* transition bands of trans-azobenzene, respectively. UV light irradiation decreased the intensity of the π-π^* transition band at 355 nm and increased the intensity of the n-π^* transition band at 434 nm. The π-π^* transition band also shifted from 355 nm to 327 nm, and the n-π^* transition band at 434 nm shifted to 440 nm. After visible light illumination, the spectrum of the azobenzene solution recovered.

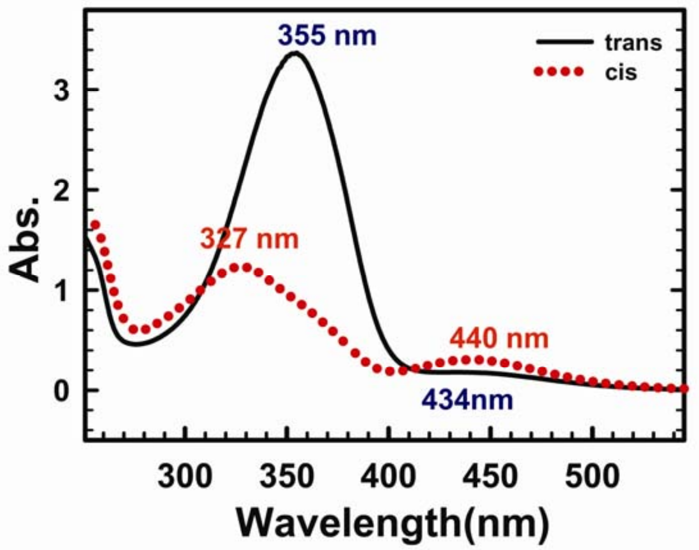


Figure S1. UV/vis absorption spectra of CF3AZO in CH_2Cl_2 solution.

Preparation of porous nanostructured substrates.

Porous nanostructured surfaces with multi-layered structures were fabricated on negatively charged silicon wafers using the layer-by-layer (LbL) technique, such that the polyelectrolyte PAH and SiO_2 nanoparticles ($d \approx 11$ nm) functioned as the polycations and polyanions, respectively. Prior to the first deposition of SiO_2 nanoparticles, a $(PAH/PSS)_5/PEI$ prelayer was deposited onto each freshly treated Si wafer to enable the subsequent preparation of a dense SiO_2 nanoparticle layer. The $(PAH/PSS)_5/PEI$-coated Si wafer was then immersed alternately in a 0.05 wt% SiO_2 nanoparticle dispersion and a PAH solution, 5 min for each incubation, then washed three times for 1 min with Milli-Q water. Previous experience with nanostructured surface preparation based on LbL deposition suggested that the best surfaces were prepared with ten deposition cycles. After deposition, first an adhesion layer of titanium (2 nm) then a conducting film of gold (10 nm) was deposited onto the topmost layer of the silica nanoparticles by thermal evaporation.

Immobilization of azobenzene derivatives onto the rough substrate. The gold surfaces of the porous substrates were functionalized by immersion in a 1 mM ethanolic solution of 11-amino-1-undecanethiol-hydrochloride overnight, then washed sequentially with ethanol, chloroform, and water to remove excess reagent. The photoreversible moieties were introduced by incubating the amine-modified substrates in an ethanolic solution of 1 mM CF3AZO, in the presence of 10 mM N-ethyl-N-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC). The reaction was carried out in an airtight vessel, at room temperature, with gentle shaking for 10 h. The substrates were removed from the solution, washed sequentially with ethanol and water to remove unbound azobenzene, and dried under vacuum for 1 h.

Characterizations: The water contact angles on the substrates were measured by a contact angle goniometer (SEO300A) at ambient temperature, under conditions of saturated humidity, and were recorded immediately after placing an aqueous droplet on the sample. Photoisomerization of the azobenzene derivatives was induced by illumination from a 500 W high pressure Arc-Xe lamp (Oriel) light source. Light was passed through a 10 cm IR water filter and a cut-off filter ($\lambda \sim 365$ nm for UV or $\lambda > 420$ nm for visible light irradiation), and the filtered light was focused onto the substrate. The samples were placed at a distance of 10 ~ 15 cm from the lamp for 10 min under UV or for a specified time under visible light illumination at room temperature.

The surface potential was measured using a secondary electron emission spectrometer at the 2B1 and 4B1 beam lines at the Pohang Accelerator Laboratory (Korea). The onset of photoemission, which accompanied photoinduced isomerization with a simultaneous increase of the surface dipole moment of the tethered azobenzene molecules on the surface, was measured under conditions in which a negative bias (-20 V) was applied to the sample to avoid the work function of the detector. The surface chemical status of the substrates was confirmed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 220i VG instrument, take-off angle 35°). The adsorption behavior of alkanethiols onto the substrates was detected with a quartz crystal analyzer (QCA) (Stanford Research Systems) by *in situ* monitoring of the frequency of the electrode (f). For this experiment, nanostructured quartz crystals were cleaned and prepared following the same preparation procedure for the modification of the silicon wafer described above. Subtracting f_0 from f, we obtained the time-dependent frequency change Δf ($= f - f_0$) of the flat and rough quartz crystals. The principals of QCA are well described elsewhere.