

## Electronic Supplementary Information

### A facile method to immobilize cucurbituril on surfaces through photocrosslinking with azido groups

#### 1. Experimental details

##### 1.1 Materials

3-Aminopropyltriethoxy-silane (APTES) was purchased from Alfa Aesar. Acridine orange base (AO) was obtained from Aldrich. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide, 1-adamantanecarboxylic acid (Ad), and 4-azidobenzoic acid (PA) were purchased from J&K. CB[7] was purchased from Strem Chemicals UK, Ltd. Silicon wafer was obtained from China Electronics Technology Group Corporation and quartz substrates were obtained from Beijing Zhongcheng Quartz Glass Co., Ltd.

##### 1.2 Instruments

Fourier transform infrared (FTIR) spectra and attenuated total reflection (ATR) spectra were collected with a Nicolet IS5. UV-visible spectra were obtained using a Hitachi U-3900H. NMR spectra were recorded on a Bruker DRX spectrometer (300 MHz,  $^{13}\text{C}$ ). Thermogravimetric (TG) analysis was conducted on a TA Q500 at a heating rate of 10 °C/min in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos Axis Ultra system with a monochromatized Al K $\alpha$  radiation at 1486.6 eV as the X-ray source. The contact angle was characterized on an OCA20 instrument (Data Physics Instrument GmbH, Filderstadt). Photochemical patterning was conducted with photolithography equipment (G-25) (Chengdu Xinnanguang Mechanical Equipment Co., Ltd, China). Fluorescence images were obtained with TCS SP5 II confocal fluorescence microscope from Leica, and excitation wavelength of 488 nm was used.

##### 1.3 Synthesis and surface modification of SiO<sub>2</sub> nanoparticles

SiO<sub>2</sub> nanoparticles were synthesized following conventional protocols. Briefly, 200 mL ethanol, 4 mL deionized water and 9 mL ammonium hydroxyl (25%) were added into a 500 mL

round-bottom flask. After stirring for 5 min, 6 mL TEOS was added dropwise. Then the mixture was kept at 40 °C in the water bath with stirring for 4 h. Another 4 mL TEOS was then added dropwise followed by stirring for 12 h. Silica nanoparticles with –OH groups were obtained and then purified by centrifuge and redispersion for three times.

CB[7] was introduced onto the surface of the SiO<sub>2</sub> nanoparticles in three steps. First, amido groups were introduced onto the surface: 0.6 mL of APTES was dissolved in 20 mL ethanol and the solution was added dropwise into the dispersion containing SiO<sub>2</sub> nanoparticles, followed by stirring for 24 h at 75 °C. The nanoparticles were collected by centrifugation and re-dispersed in water, and the cycle was repeated three times for purification. Second, an aqueous solution containing 2.0 mmol PA and an equal amount of EDC were added into the aqueous dispersion of the nanoparticles, followed by stirring for 48 h. Then the nanoparticles were purified by centrifugation and re-dispersed three times. Third, 20 mg of nanoparticles powder and 2 mg of CB powder were put in agate mortar and mixed with pestle. The mixture was exposed to UV irradiation by high-pressure mercury (200 W) of photolithography equipment with an intensity of 7.9 mW cm<sup>-2</sup> at a distance of 10 cm for 10 min, whose rays are combination of 365 nm/405 nm/436 nm. Afterwards, the nanoparticles were washed by water and purified as stated previously.

#### 1.4 Immobilization of CB[7] on silicon substrate

Silicon sheet was cleaned with piranha solution (H<sub>2</sub>SO<sub>4</sub>(v): (30%H<sub>2</sub>O<sub>2</sub>)(v) = 7:3, caution, highly corrosive!) for 1 h, washed with copious amounts of water and dried by N<sub>2</sub>. Then the silicon sheet was immersed in a toluene solution of 0.1 mmol APTES for 10 h, washed with toluene and ethanol three times and dried. As the next step, the sheet was immersed in 40 mL aqueous solution containing 100 mg PA and an equal molarity of EDC for 48 h, cleaned with water three times and dried. The sheet was covered with an aqueous solution of CB[7] (0.4 mg/mL), dried in a desiccator with phosphorus pentoxide for 12 h, and irradiated under UV light from a commercially available 200 W high-pressure mercury lamp for 10 min. The sheet was then carefully washed with copious amounts of water and dried by N<sub>2</sub>.

#### 1.5 Patterning of quartz sheet/silicon with CB[7] using photolithography

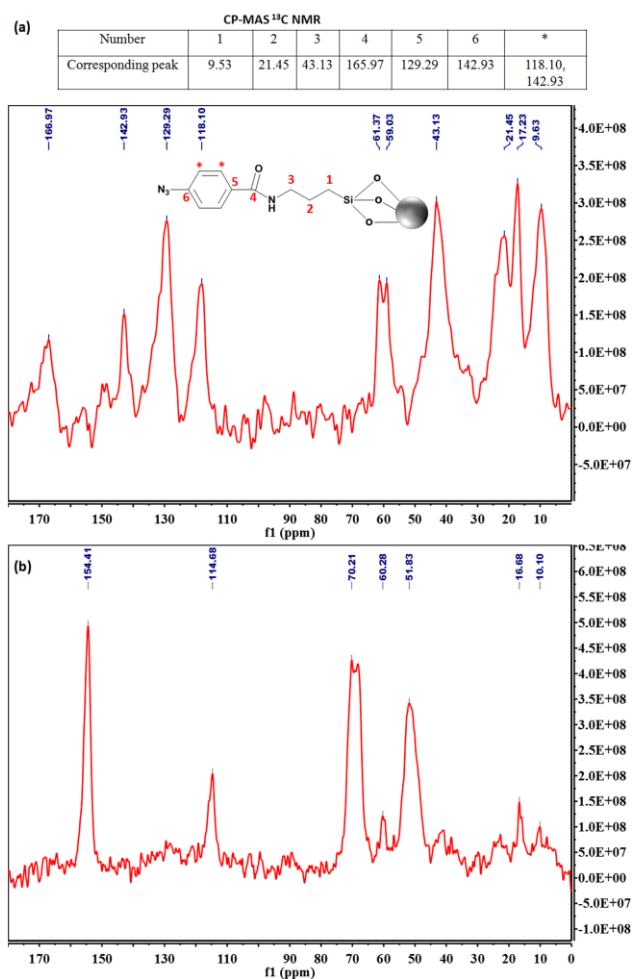
The substrate was modified with APTES and then azide groups as stated above. Then the

substrate was irradiated with UV light ( $7.9 \text{ mW cm}^{-2}$ , 10 min) through a photolithography mask (the pattern was squares of  $90 \mu\text{m} \times 90 \mu\text{m}$ ). The area exposed to UV light was deactivated. Then aqueous solution of CB[7] (0.4 mg/mL, 0.8 mL) was dripped onto the substrate ( $1 \text{ cm} \times 1 \text{ cm}$ ). The substrate was then dried in a desiccator with phosphorus pentoxide for 12 h, and irradiated under UV for 10 min.

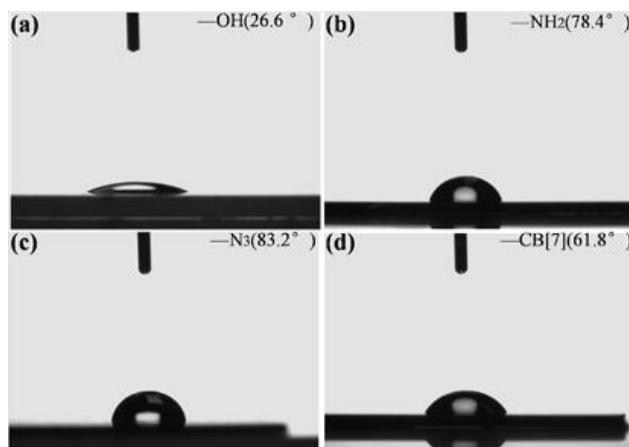
### 1.6 Molecular recognition towards AO and 1-adamantanecarboxylic acid (Ad)

Molecular recognition towards AO was conducted by immersion of the substrate into a solution of AO in phosphate buffer for 30 min, washed with copious amounts of water, and dried by  $\text{N}_2$ . Molecular recognition of Ad was conducted by immersion of the substrate into an aqueous solution of Ad (1 mg/mL) for 0.5 h, then washing with copious amounts of water and drying.

## 2. CP-MAS $^{13}\text{C}$ NMR spectra and CA measurement of different functional groups attached to the silicon nanoparticles



**Figure S1.** (a) CP-MAS  $^{13}\text{C}$  NMR of silica particles after modification with  $-\text{N}_3$  groups; (b) CP-MAS  $^{13}\text{C}$  NMR of silica- $\text{N}_3$  particles with immobilized CB[7].

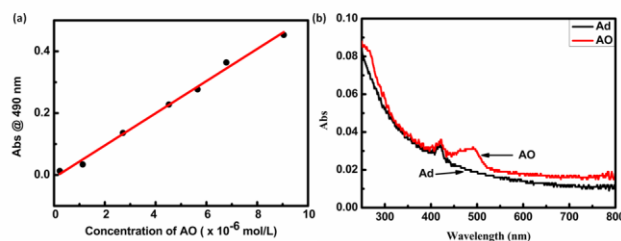


**Figure S2.** The contact angles of the silicon sheet with different surface functionalities. a) before modification; b) modified by APTES; c) modified with azido groups; d) after immobilization of CB[7]

### 3. Calculation of surface coverage on quartz sheet

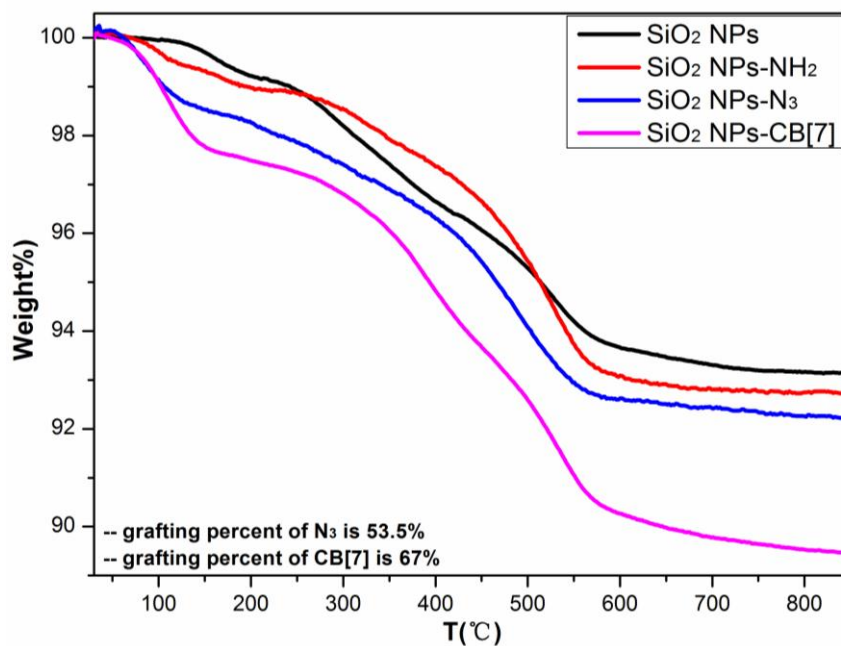
The surface coverage of CB[7] on the quartz sheet was obtained by calculating the surface coverage of AO, given the fact that a single AO molecule could fit into the cavity of one CB[7] molecule. Taking advantage of the reversibility of the host-guest interactions, AO immobilized through CB[7] were removed by rinsing the quartz sheet into an aqueous solution (9 mL) of competing guest Ad with a concentration of 1 mM. In this process the AO should mostly be replaced by Ad, due to the large binding constant between Ad and CB[7], as well as the high concentration of Ad in the solution. Then, the concentration of AO in the resultant solution was measured with UV-visible spectra. An increase in the absorbance of 0.012 was obtained after the competitive reaction. To determine the amount of AO responsible for the absorbance of 0.012, a standard curve of absorbance-concentration for AO solution was generated. A relationship of  $A = -0.00859 + 7.256 \times 10^4 c$  was obtained, where A denotes absorbance and c the concentration of AO. Using this relationship, the amount of AO in 9 mL solution responsible for the absorbance of 0.012 was calculated to be  $2.55 \times 10^{-9}$  mol. The surface area of the quartz sheet ( $0.1 \times 1 \times 3$  cm), without considering roughness, was  $6.8 \text{ cm}^2$  times the double faces. Thus a surface coverage of

$5.24 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ , equalling  $3.15 \times 10^{14} \text{ molecules} \cdot \text{cm}^{-2}$ , was obtained.



**Figure S3.** (a) The standard curve of UV-visible absorbance-concentration for AO solution;  
(b) UV-visible spectra of the after immersed in Ad and AO.

#### 4. Investigation of reaction efficiencies of different functional groups attached to the silicon nanoparticles by TGA



**Figure S4.** TGA analysis of nanoparticles with different functional groups introduced.