Supporting information

Optical Detection of Anions using N-(4-(4-nitrophenylazo)phenyl)-N'-propyl thiourea Bound Silica Film.

Ryo Kato,[a] Akinori Kawai,[b] and Toshiaki Hattori[b,c]

a Cooperative Research Facility Center, Toyohashi University of Technology, Toyohashi, 441-8580, Japan
b Department of Materials Science, Toyohashi University of Technology, Toyohashi, 441-8580, Japan
c Department of Electrical & Electronic Information Engineering, Toyohashi University of Technology,
Toyohashi, 441-8580, Japan

Supporting information includes:

Surface state of the anion sensing silica film

Surface state of the all anion sensing silica films was investigated by scanning electron microscopy (SEM) (Nikon ESEM-2700). Figure S1 show the SEM image of surface (a) and cross section (b) of film AR on glass substrate. We confirmed that all the film surfaces were flat and that no cracks or particles were apparent. SEM image of the cross section of the film shows that thickness of these films was about 10 μm.

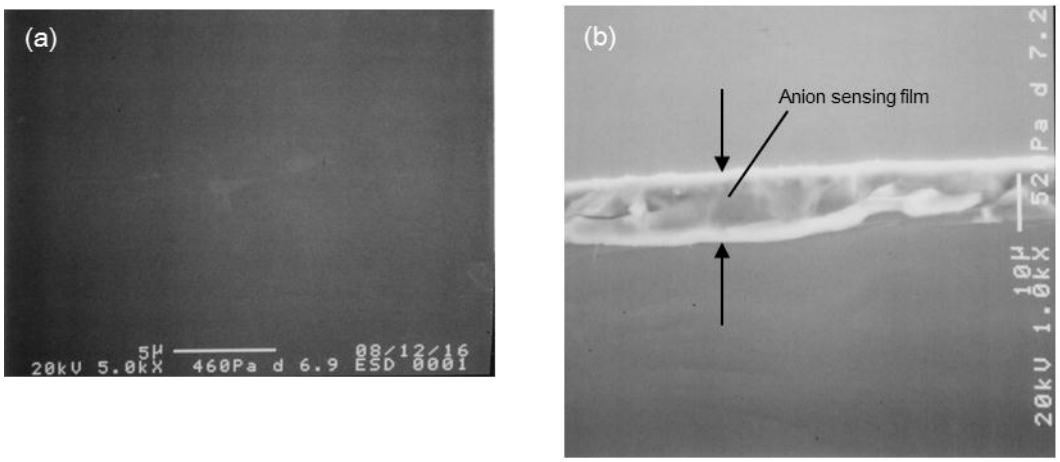

Figure S1 SEM images of (a) surface and (b) cross section of silica film AR

Surface state of the all anion sensing silica films was also investigated by confocal laser scanning microscope(CLSM) and AFM (Olympus LEXT-OLS3500). Figure S2 shows the CLSM image of the surface of film AR on glass substrate. There are many small hills which cannot observe with SEM measurement on the film. Figure S3 shows the AFM image of surface of the film AR. Many small hills and pillars exist on surface of the film AR. Small hills have 0.6-1.0 μm of diameter and 6.8-14.9 nm of height in this AFM image (line A-B). This hills the same object which observed with CLSM measurement. Pillars have 0.1-0.2 μm of diameter and 7.5-30 nm of height in this AFM image (line C-D).

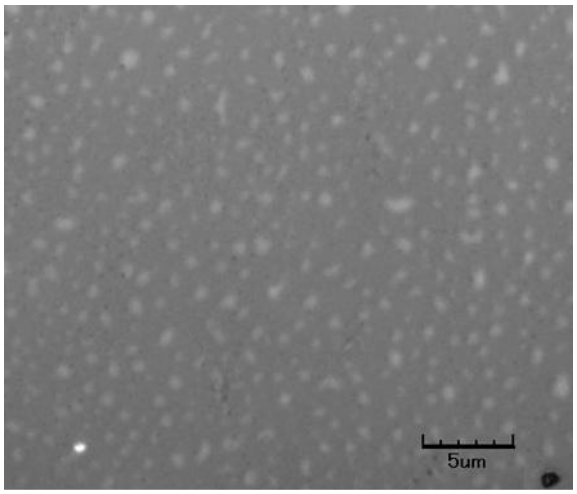

Figure S2. CLSM image of the surface of film AR on glass substrate.

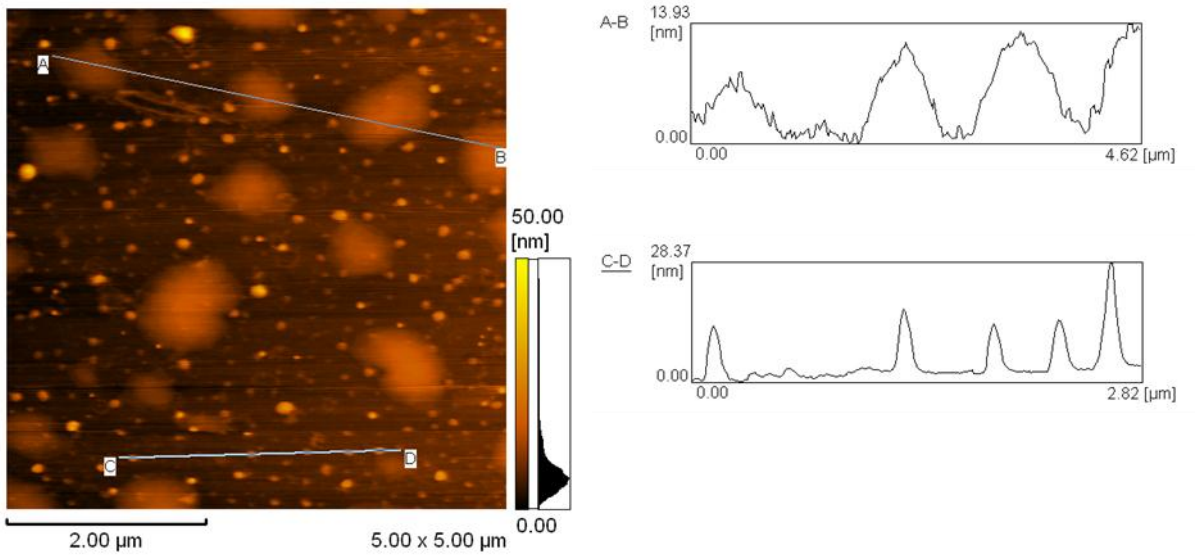

Figure S3. AFM image of the surface of film AR on glass substrate.

*NMR titration of **1** and acetate in CD_3CN*

1:1 dilution measurement was carried out to investigate the hydrogen-bond formation behavior between **1** and acetate anion. Figure S4 shows changing the ^{1}H-NMR spectrum on diluting the **1** : acetate = 1 : 1 mixture in CD_3CN. When solution was diluted to 0.1 mM, upfield shift of two NH peaks were observed. This shift shows the dissociation of hydrogen bonding between **1** and acetate is occurred and NH peaks are reversed from complex-form thiourea to free thiourea. These changing cannot observe if proton transfer is occurred between **1** and acetate.

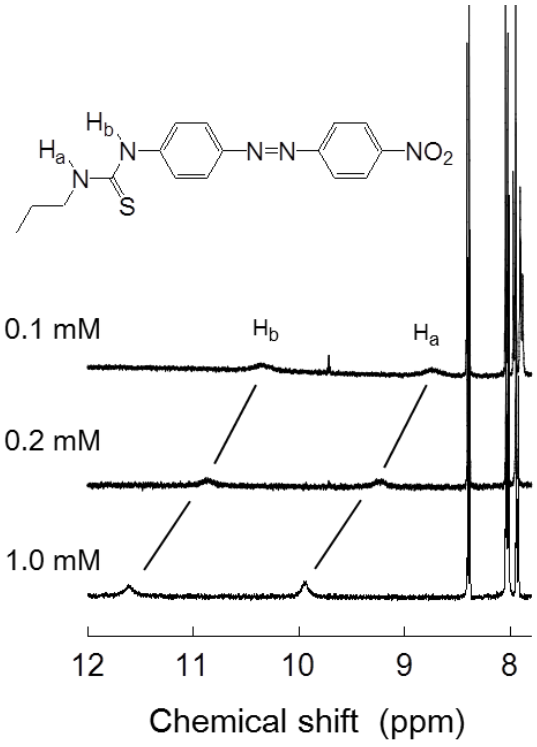

Figure S4. 1:1 dilution measurement of **1** and acetate in CD_3CN.

TIR absorption spectra titration of substrate AR and acetate, dihydrogenpohsphate and chloride

Figure 5S shows the changing in the absorbance of anion sensing silica film AR on addition of various concentrations of anions. Fitting curve was calculated on the assumption that anion receptor **2** reacts with anions with a 1:1 stoichiometry. Deviation of data points from fitting curve seems to be random.

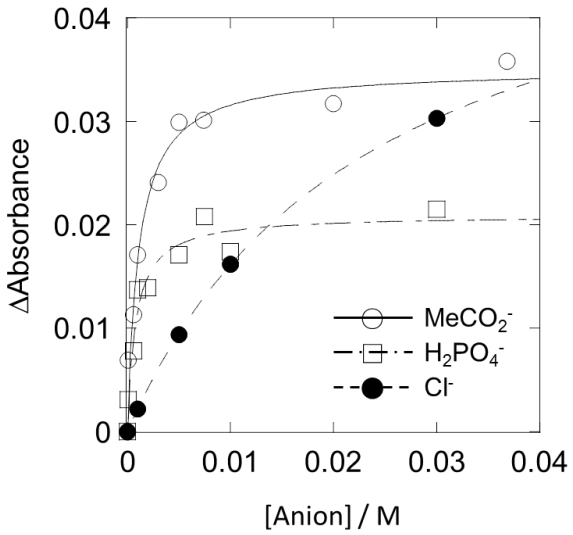

Figure S5. Changing in the absorbance of anion sensing silica film AR on addition of various concentration of $MeCO_2^-$ (open circle), $H_2PO_4^-$ (open square) and Cl^-(solid circle).