# Electronic Supporting Information

## Study of pH-dependence Shrink and Stretch of Tetrahedral

## **DNA Nanostructure**

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## **Tetrahedron assembling**

Six single-stranded DNA were purchased from TAKARA, the sequences are listed in table 1. We consulted the tetrahedron assembling method of Turberfield's group.<sup>[16]</sup> The tetrahedral DNA nanostructure (TDN) with i-motif was hierarchically assembled from three thiolated DNA fragments of 55 (55-nt) nucleotides (No.2, 3, 4) and one i-motif-containing DNA fragment of 80-nt (No.1), and the sequence 2,3,4,5 were assembled to the TDN structure. 2µL of each single-stranded DNA (50µM) were added into 42µL Tris-MgCl<sub>2</sub> solution (Tris 10mM, MgCl<sub>2</sub> 50mM, pH8). Then put this solution into Life Express Thermal Cycler (Hangzhou Bioer Technology Co., Ltd)

and the TDN was assembled under the condition of  $95\,^\circ\!\!\mathbb{C}$  for 10minutes and cooled

rapidly to  $4\,^\circ\!\!\mathbb{C}$  for 30minutes. The final concentration was  $2\mu M.$ 

## Sequences of single-stranded DNA used in this work

Table 1 The sequences of six single-stranded DNA used in this work



The sequence of the DNA double helix is called BRCA (SH)-GAGCATACATAGGGTTTCTCTTGGTTTCTTTGATTATAATTCATAC), a type of gene order closely related to the breast cancer.

## The inverted fluorescence microscope imaging

The tetrahedral DNA nanostructure with fluorescence (Cy3-TDN) was hierarchically assembled from one Cy3–containing DNA fragment (No.6) and three thiolated DNA fragments of 55 nucleotides (No.2, 3, 4), and the sequence of Cy3-containing DNA fragment (No.6) is the same with No. 5. We took 4 DNA fragment (No.2, 3, 4, 6) which were not well assembled to TDN as the blank. Then, both of the TDN which were not well assembled and the well assembled TDN were prepared by deposition of  $200\mu$ L onto freshly cleaved Au surface (the gold coated quartz crystal used in QCM), and left to adsorb to the surface for 3h, rinsed with Milli-Q water for several times. Then they were mounted on the inverted fluorescence microscope (Leica DMI 4000B) and get a clear image.

## Polyacrylamide gel electrophoresis

Polyacrylamide electrophoresis gel (40%) was run in  $1 \times$  TBE with 100V for 3h (JY600C, Junyi-DongFang Co., Ltd, China). This system was set at ice slurry to make sure the temperature maintained at 0°C. When finished, the image was visualized using a fluorescence scanner (Tocan240, China).

### **AFM** imaging

Samples were prepared by deposition of  $100\mu$ L onto freshly cleaved Au surface (the gold coated quartz crystal used in QCM), and left to adsorb to the surface for 3h, rinsed with Milli-Q water for 3 times. Then they were mounted on a Veeco Multimode AFM Nanoscope3. Adjust the AFM parameters and get a clear image.

### Quartz crystal technique

In this study, we used QCM D-300 (Q-sense) to get the structure changes of DNA nanocomplexes. A freshly cleaned quartz crystal with the fundamental resonant frequency of 5MHz was installed in the liquid cell. Gold films evaporated on the surfaces of the quartz crystals acting as the electrodes were used as the adsorption substrates. In room temperature, we dropped 100 $\mu$ LDNA solution (1 $\mu$ M) on the gold coated quartz crystal surface and let it absorb overnight. Then the DNA structures were immobilized on the gold electrode by thiol group and the surface was rinsed with the PBS buffer for several times to remove the unabsorbed DNA molecular. Then the crystal was installed in the flow cell, and the PBS buffer with pH 8.5 flowed into the liquid cell. Afterwards, after the frequency shift and dissipation factor reached a stable value, we left it for about 10minutes, and then injected the PBS buffer of pH 4.5. The circle is repeated for several rounds.

#### Scaling measurement of Au nanoparticle-TDN

The scale was measured using Zetasizer NanoZS (Malvern Co., Ltd; Cell type: ZEN0040). The setup parameters were as follows: material: Au; refractive index:

0.290; absorption: 0.010; dispersant: PBS; temperature: 25°C; viscosity: 0.8872cP; RI:

1.330. Au nanoparticle (13nm, 3nM) was synthesized in our lab. To investigate the pH stimuli-responsive behaviour of the different construction of DNA, we measured the scale of Au nanoparticle in neutral, Au nanoparticle-double stranded, Au nanoparticle-TDN and Au nanoparticle-TDN-i-motif in pH4.5 and pH8.5. First, we added 1 $\mu$ l SH-(PEG)<sub>7</sub>-OCH<sub>3</sub> (1mg/ml) into 1ml Au nanoparticle solution (13nm, 3nM), and approximately 30 minutes later, TDN or TDN i-motif solution was added into the Au nanoparticle solution and was modified for 3 hours at least. Au nanoparticles (AuNPs) with different constructions of DNA were synthesized in neutral and then centrifuged (13000rpm, 15minutes) to remove the unbound DNA scaffold and SH-(PEG)<sub>7</sub>-OCH<sub>3</sub>. Finally, AuNPs were resuspended in the phosphate buffer at the concentration of 10nM with pH 4.5 or pH 8.5.



Fig.1./Measured resonant frequency shift of the quartz crystal resonator as the function of time (a) TDN i-motif; (b)TDN; (c) DNA-double helix.



Fig.2./The inverted fluorescence microscope imaging

After washing over 20 times, the fluorescence intensity reduced tinily because the photo bleaching, but the TDN was still locked on the surface and not affected by washing.



Fig.3./AFM image of Au surface before (a, c) and after (b, d) modified TDN



Fig.4. /AFM image of mica surface before (a) and after (b) modified TND

DNA tetrahedron on mica in solution was imaged with the taping mode AFM. However, although it failed to show the tiny changes of the DNA structures, the height of the TDN is about 2-3nm. That demonstrates the TDN was successfully assembled and can securely absorb on the gold surface.



**Fig.5./Schematic of the DNA molecular modified gold nanoparticle surfaces** (a) TDN i-motif; (b) TDN; (c) DNA double helix.

#### Quantification of TDN film thickness by QCM-D:

Four overtones (first, third, fifth and seventh) were used to model the thickness using the Voigt model implemented in the software (Q-Tools software 301 version 2.1, Q-Sense, Sweden). The saturated values of  $\Delta f$  and  $\Delta D$  in the thick limit of an adsorbed layer can be derived straightforwardly as the following: <sup>[32]</sup>

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q} \left[ \frac{\eta_3}{\delta_3} + \sum_{j=1,2} (\rho_j h_j \omega - 2(\frac{\eta_3}{\delta_3})^2 \frac{\eta_j \omega^2 h_j}{\mu_j^2 + \eta_j^2 \omega^2}) \right] \quad (1)$$
$$\Delta D \approx \frac{1}{2\pi\rho_q h_q f} \left[ \frac{\eta_3}{\delta_3} + \sum_{j=1,2} 2(\frac{\eta_3}{\delta_3})^2 \frac{\mu_j \omega h_j}{\mu_j^2 + \eta_j^2 \omega^2} \right] \quad (2)$$

The changes of the resonant frequency ( $\Delta f$ ) and the dissipation factor ( $\Delta D$ ) are related to the viscosity  $\eta$  and shear modulus  $\mu$  of the adsorbed layer, where *h* and  $\rho$  are the thickness and density of the adsorbed layer, respectively. Considering two thin viscoelastic overlayers of thickness  $h_j$  (j=1, 2) in a bulk Newtonian liquid, based on Eqs. (1) and (2) it follows that for ultrathin films, the contribution of the film is small in comparison with the bulk liquid.  $\rho_q$  and  $h_q$  are the density and thickness of quartz crystal. All measured overtones were included in the fitting routine.