

Supporting Information

Materials: Multiwalled carbon nanotubes (MWNTs, $\phi = 10\text{-}30\text{ nm}$) were purchased from Nanotech Port Co. Ltd. (Shenzhen, China). Aluminum hydride (LiAlH_4) and deoxycytidine Monophosphate (dCMP) was purchased from Aldrich (St. Louis, MO). Diethylazodicarboxylate (DEAD) was purchased from Alfa (Ward Hill, MA). Phthalimide and hydrazine ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 85%) were obtained from Beijing Chemicals Inc (Beijing, China). All other reagents were of analytical reagent grade.

Chemical modification of SWNTs and MWNTs: The carboxyl-modified SWNTs or MWNTs were prepared by sonicating the primitive SWNTs in a 3:1 vol/vol solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) for 24 h at 35–40 °C, and washed with water, leaving an open hole in the tube side and functionalizing the open end of SWNTs with carboxyl group to increase their solubility in aqueous solution (1-7).

The hydroxyl-modified SWNTs were obtained by reducing carboxyl-modified SWNTs using lithium aluminum hydride (LiAlH_4) in anhydrous tetrahydrofuran (THF). After reduction, samples were successively washed with methanol, diluted HCl, and water (7,8).

The aminomethyl-modified SWNTs were prepared via chemical modification of hydroxyl groups introduced on the carbon nanotube surface. Reduced SWNTs were dispersed in THF and then phthalimide was added followed by diethylazodicarboxylate (DEAD) coupling agent. The solution was sonicated for 2 h followed by stirring for 3 h. The mixture was then washed with methanol and dried at

40 °C under vacuum for 8 h. Phthalimide-modified SWNTs were obtained. These were then mixed with hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 85%), sonicated for 3 h, followed by washing with methanol and water (8).

FTIR (Figure S1, $\text{KBr}, \text{cm}^{-1}$): SWNT-COOH, 3500 (s, broad peak), 2800–3000 (w), 1726 (ms), 1385 (w), 1231 (s); SWNT- CH_2 -OH, 3434 (s), 2920(w), 2848 (w), 1633 (ms); SWNT- CH_2 - NH_2 , 3400 (ms, broad peak), 2800–3000 (w), 1571 (s), 1190 (ms).

Reference

1. Li, X., Peng, Y.H. and Qu, X.G. (2006) Carbon nanotubes selective destabilization of duplex and triplex DNA and inducing B-A transition in solution. *Nucleic Acids Res*, **34**, 3670-3676.
2. Li, X., Peng, Y.H., Ren, J.S. and Qu, X.G. (2006) Carboxyl-modified single-walled carbon nanotubes selectively induce human telomeric i-motif formation. *Proc. Natl Acad. Sci. USA*, **103**, 19658-19663.
3. Peng, Y.H., Li, X., Ren, J.S. and Qu, X.G. (2007) Single-walled carbon nanotubes binding to human telomeric i-motif DNA: significant acceleration of S1 nuclease cleavage rate. *Chem. Comm.*, 5176-5178.
4. Zhao, C., Song, Y.J., Ren, J.S. and Qu, X.G. (2009) A DNA nanomachine induced by single-walled carbon nanotubes on gold surface. *Biomaterials*, **30**, 1739-1745.
5. Zhao, C., Ren, J.S. and Qu, X.G. (2008) Single-walled carbon nanotubes binding to human telomeric i-Motif DNA under molecular-crowding conditions: more water molecules released. *Chem. Eur. J.*, **14**, 5435-5439.
6. Peng, Y.H., Wang, X.H., Xiao, Y., Feng, L.Y., Zhao, C., Ren, J.S. and Qu, X.G. (2009) i-Motif quadruplex DNA-based biosensor for distinguishing single- and multiwalled carbon nanotubes. *J. Am. Chem. Soc.*, **131**, 13813-13818.
7. Zhao, C., Peng, Y.H., Song, Y.J., Ren, J.S. and Qu, X.G. (2008) Self-assembly of single-stranded RNA on carbon nanotube: Polyadenylic acid to form a duplex structure. *Small*, **4**, 656-661.
8. Campbell, J.F., Tessmer, I., Thorp, H.H. and Erie, D.A. (2008) Atomic force microscopy studies of DNA-wrapped carbon nanotube structure and binding to quantum dots. *J. Am. Chem. Soc.*, **130**, 10648-10655.

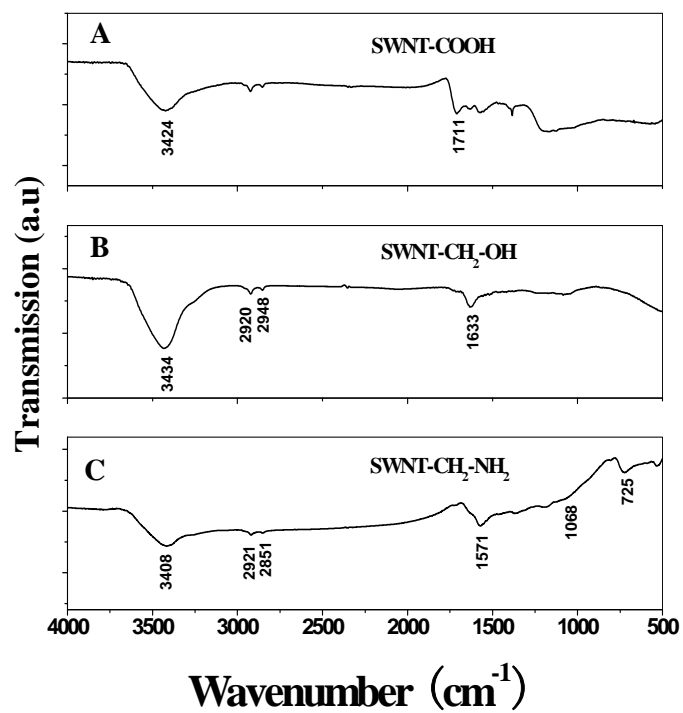


Figure S1. FTIR spectra of modified-SWNT: (A) carboxyl-modified SWNT (SWNT-COOH); (B) hydroxymethyl-modified SWNT (SWNT-CH₂OH); (C) aminomethyl-modified SWNT (SWNT-CH₂NH₂).

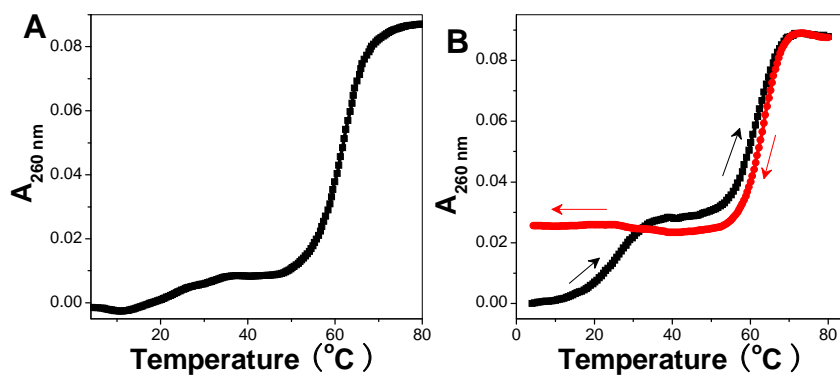


Figure S2. (A) d(AG)d(CT) at pH 5.5 (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl). (B) Melting and cooling profiles: d(AG)d(CT) in the presence of $10 \mu\text{g}\cdot\text{mL}^{-1}$ SWNTs in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl/pH 6.5). Arrows indicate directions of temperature changes (heating or cooling). Melting profile: at this DNA concentration, once melted, the triplex structure does not reform.

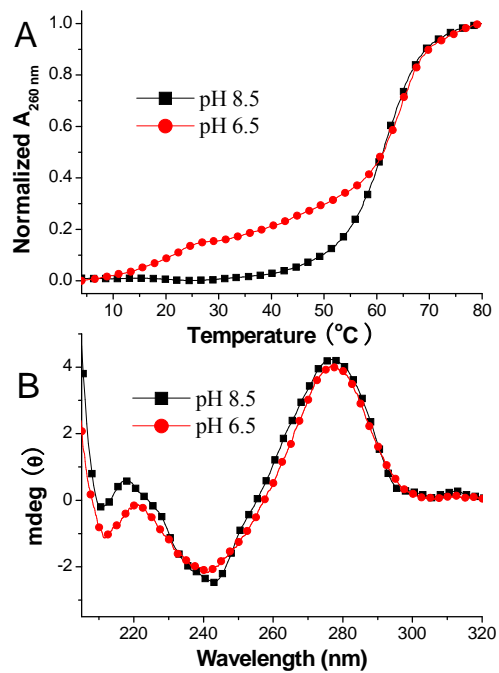


Figure S3. (A) UV melting profiles of 1 μM d(CT)·d(AG) and d(CT) in 1 mM Cacodylic, 200 mM NaCl at pH 8.5 (black) and pH 6.0 (red) (D) CD spectra of 1 μM d(CT)·d(AG) and d(CT) in 1 mM Cacodylic, 200 mM NaCl at pH 8.5 (black) and pH 6.0 (red).

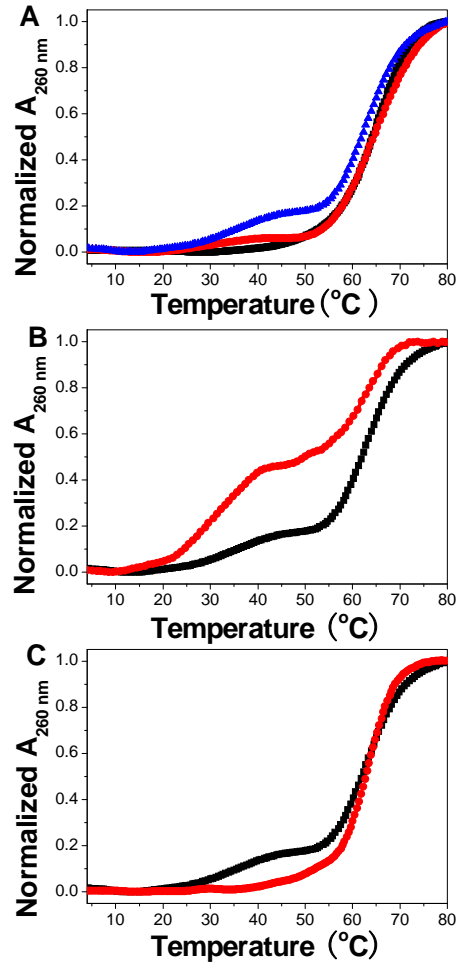


Figure S4. (A) UV melting profiles of solution containing a 1:1 stoichiometry of d(CT)·d(AG) and d(TC) in the absence (black) or presence of SWNTs: 10 $\mu\text{g}\cdot\text{mL}^{-1}$ (red), 20 $\mu\text{g}\cdot\text{mL}^{-1}$ (blue) in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl/pH 8.5). (B) To form the complete triplex need much more SWNTs than the partial triplex structure: d(CT)·d(AG) and d(TC) in presence of 20 $\mu\text{g}\cdot\text{mL}^{-1}$ SWNTs (black), d(CT)·d(AG) and d(CT) in the presence of 10 $\mu\text{g}\cdot\text{mL}^{-1}$ SWNTs (red). (C) UV melting profiles of solution containing a 1:1 stoichiometry of d(CT)·d(AG) and d(TC) in the presence of 20 $\mu\text{g}\cdot\text{mL}^{-1}$ SWNTs or 20 $\mu\text{g}\cdot\text{mL}^{-1}$ MWNTs in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl/pH 8.5).

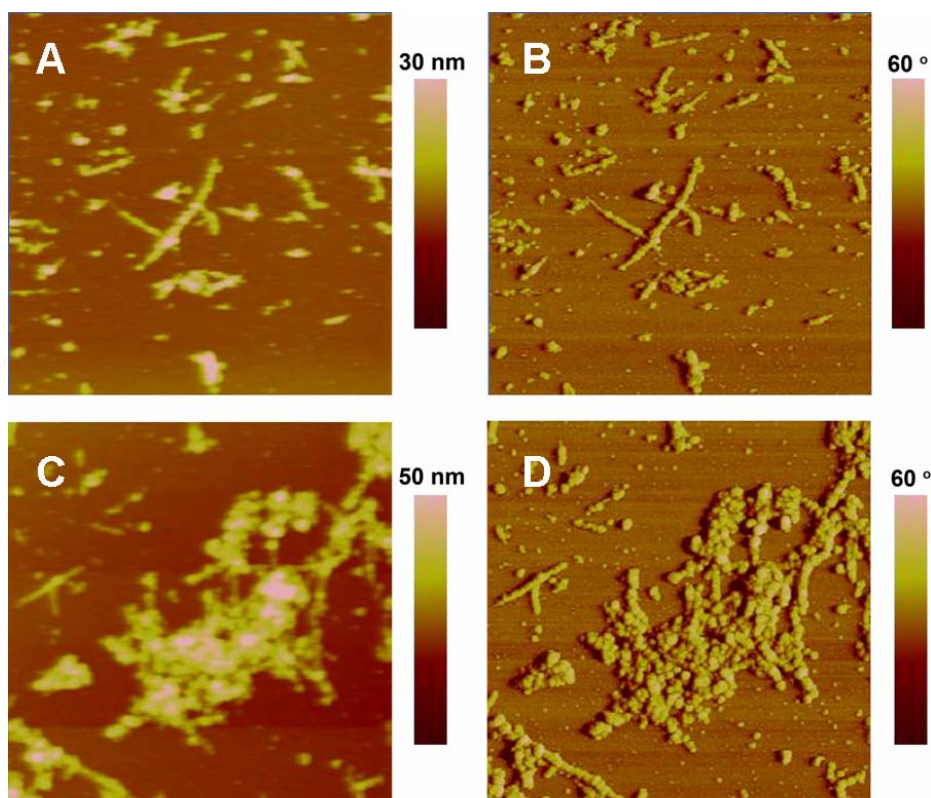


Figure S5. AFM height (left) and phase (right) images of SWNT-d(CT)-d(AG) complex at pH 6.5 (A,B) and pH 8.5 (C,D). All the experiments were carried out in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl). The images for (A–D) are $3 \mu\text{m} \times 3 \mu\text{m}$.

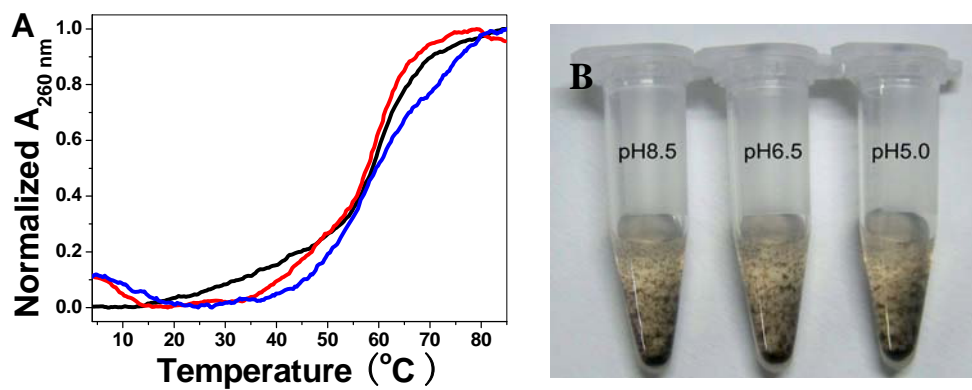


Figure S6. (A) UV melting profiles of CO-duplex in the absence (black line) or presence of SWNT-COOH: $10 \mu\text{g}\cdot\text{mL}^{-1}$ (red line), $20 \mu\text{g}\cdot\text{mL}^{-1}$ (blue line) in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl/pH 6.5). Photo images of (B) SWNT- CO-duplex at different pH values after 24 h at 4°C .

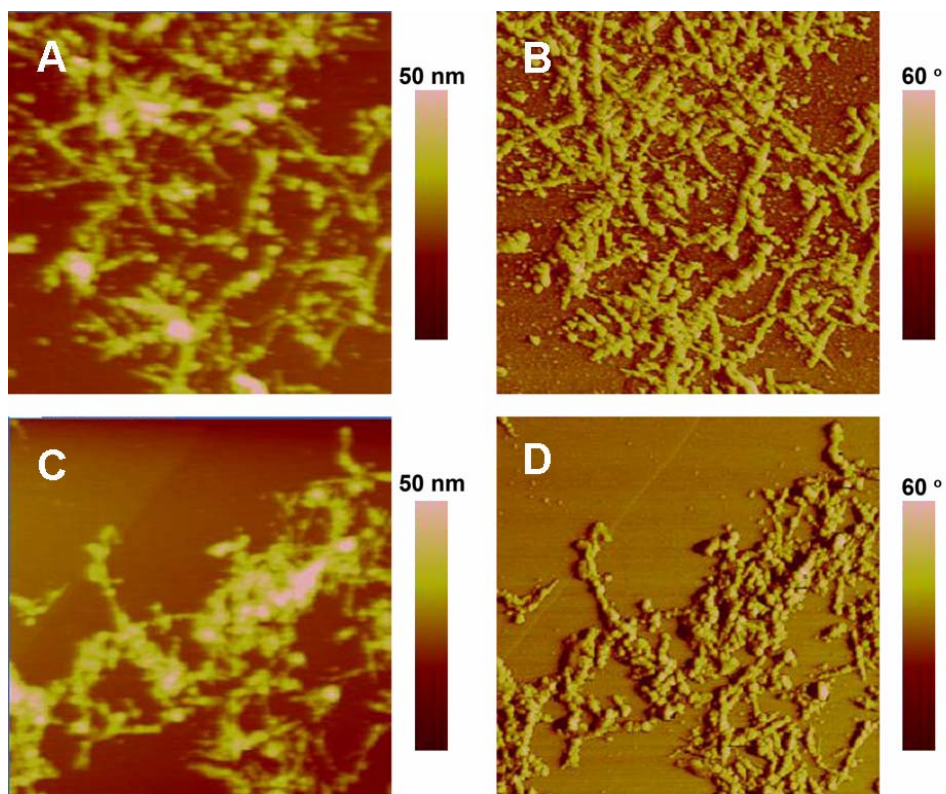


Figure S7. AFM height (left) and phase (right) images of SWNT-CO-duplex complex at pH 6.5 (A,B) and pH 8.5 (C,D). All the experiments were carried out in cacodylic buffer (1 mM cacodylic acid /sodium cacodylate/200 mM NaCl). The images for (A–D) are $3 \mu\text{m} \times 3 \mu\text{m}$.

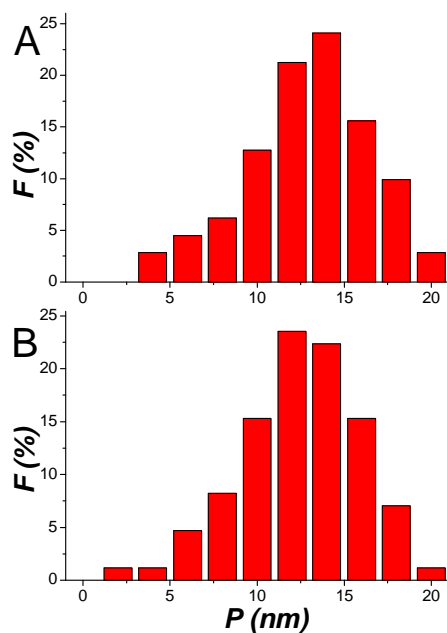


Figure S8. Distribution of the peaks of SWNT-CO-duplex at pH 6.5 (A) and pH 8.5 (B) ($n > 100$ peaks).

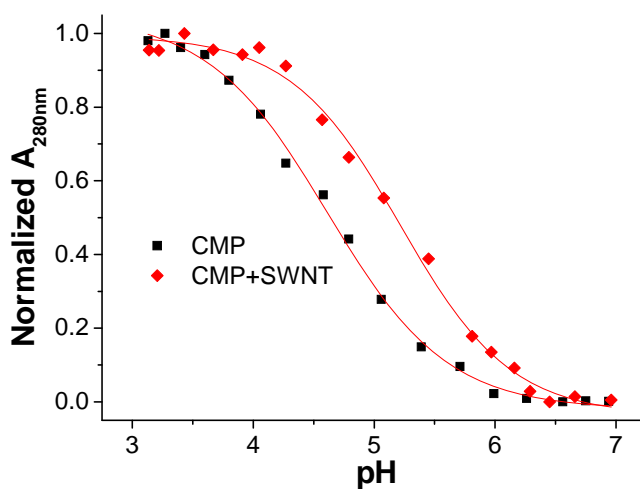


Figure S9. The plots of normalized absorption density change *versus* pH and the mid-point of the typical sigmoid curve is the pKa of dCMP. Concentration of dCMP and SWNTs are $25 \mu\text{g}\cdot\text{mL}^{-1}$ and $10 \mu\text{g}\cdot\text{mL}^{-1}$, respectively. Titration was carried out in ddH₂O.