Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Direct Observation of the Wrapping/Unwrapping of ssDNA around/from SWCNT at Single-Molecule Level: Towards Tuning the Binding Mode and Strength

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SI-1 Circular Dichroism (CD) characterization on ((GTT)3G)n/ (7, 6) CNT complex.

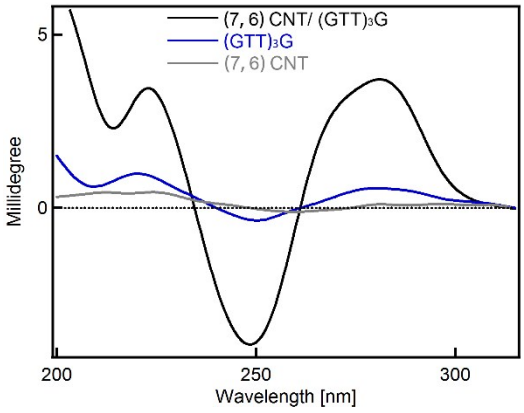

Fig. S1 Circular Dichroism (CD) characterization on pure ssDNA [((GTT)3G)n, blue trace], (7, 6) CNT (gray trace) and their complexes (black trace).

SI-2 AFM imaging on ((GTT)3G)n/ **(7, 6) CNT complex.**

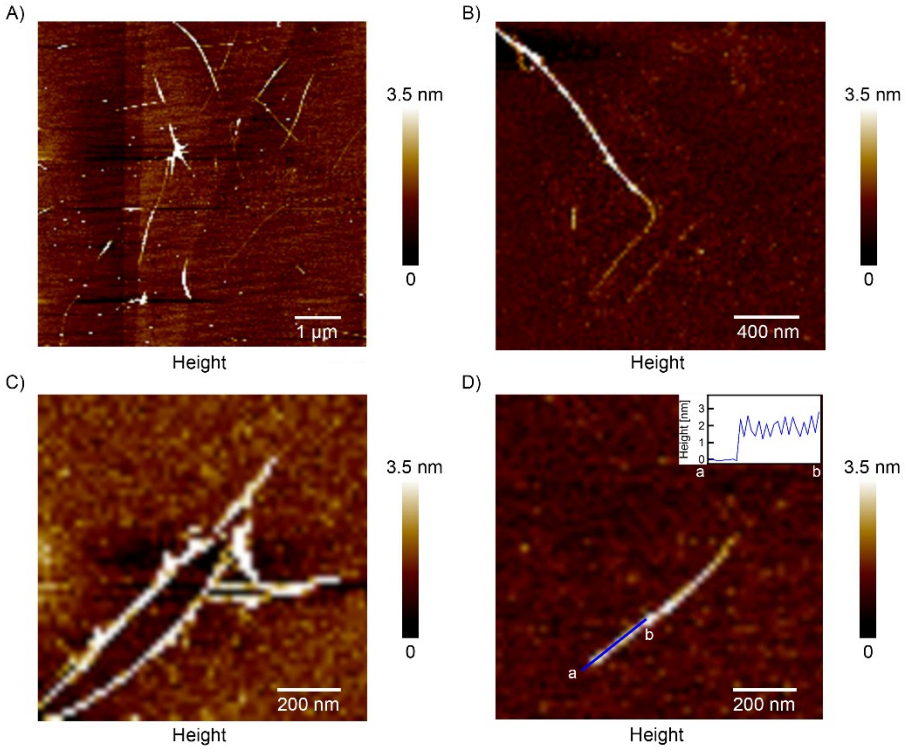

Fig. S2 AFM imaging on ((GTT)3G)n/ (7, 6) CNT complexes.

SI-3 SMFS on the ssDNA chain--((GTT)3G)n in the absence of CNT.

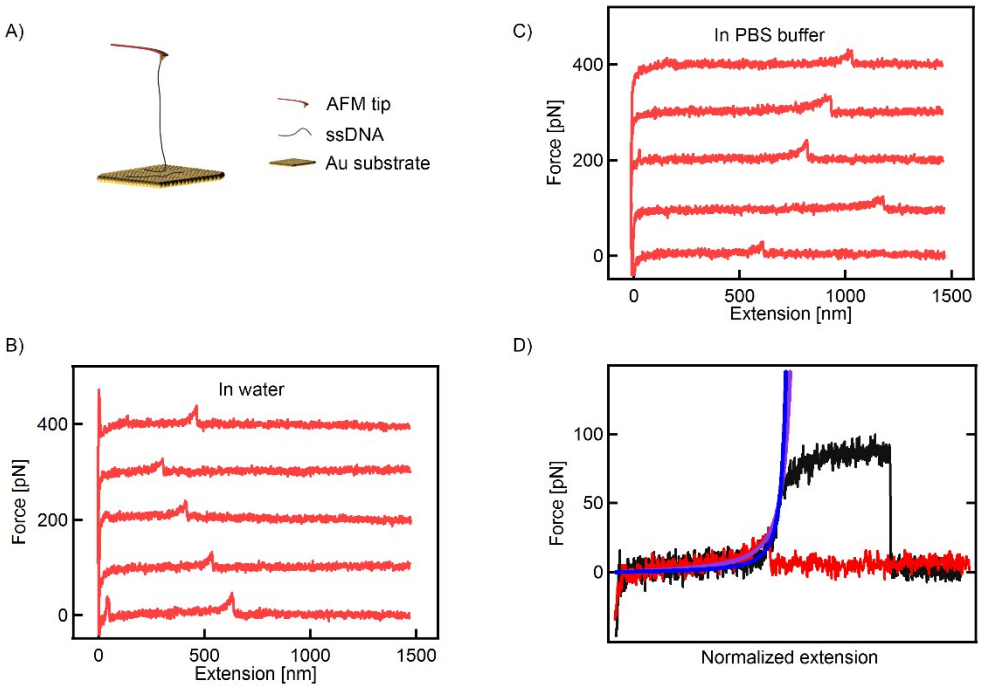

Fig. S3 (A) Schematic of SMFS on ssDNA--((GTT)3G)n. (B) Typical force-extension curves of individual ssDNA molecules with different contour lengths in water. (C) Typical force-extension curves in PBS. (D) Different elastic property of single strand DNA (red trace) and ssDNA/CNT complex (black trace). The purple and blue traces are worm-like chain fits on ssDNA and ssDNA/CNT complex, respectively (persistence length, 0.85 nm for purple lines, 2.5 nm for blue lines).

SI-4 Salt induced reversible tightening/loosening of helical structure of ssDNA on CNT.

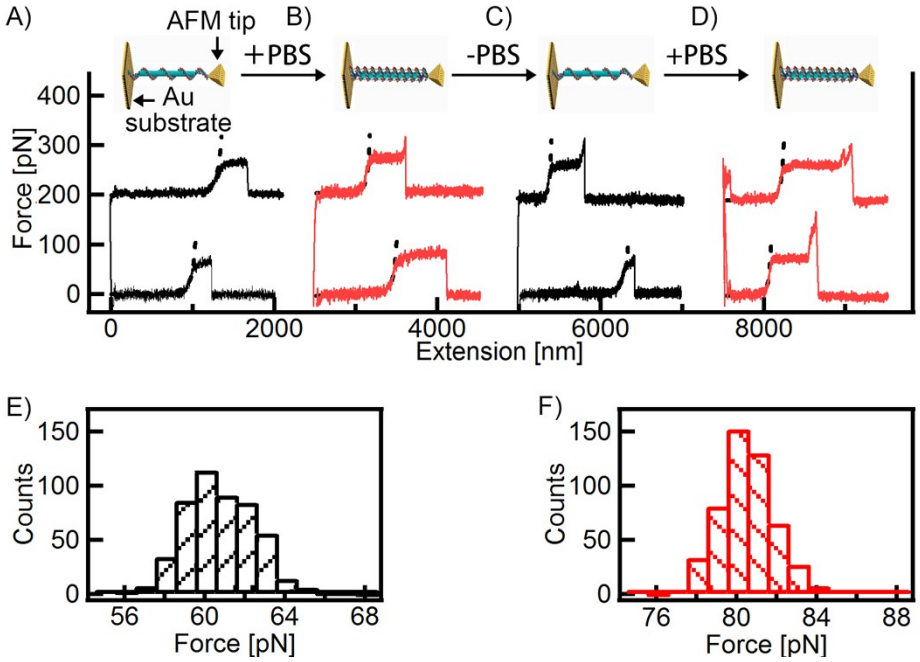

Fig. S4 Representative force-extension curves of ((GTT)3G)n/ (7, 6) CNT obtained (A) in water (black traces), (B) in PBS (red traces), (C) in water (black traces) and (D) in PBS (red traces) again in sequence on the same sample. (E) Unbinding force histograms of ((GTT)3G)n/ (7, 6) CNT in water (black, 60 pN) and (F) in PBS (red, 80 pN), respectively. The binding strength can be reversibly tuned by the buffer composition change (with or without PBS).

SI-5: Raman characterization of ((GTT)3G)n/ (7, 6) CNT

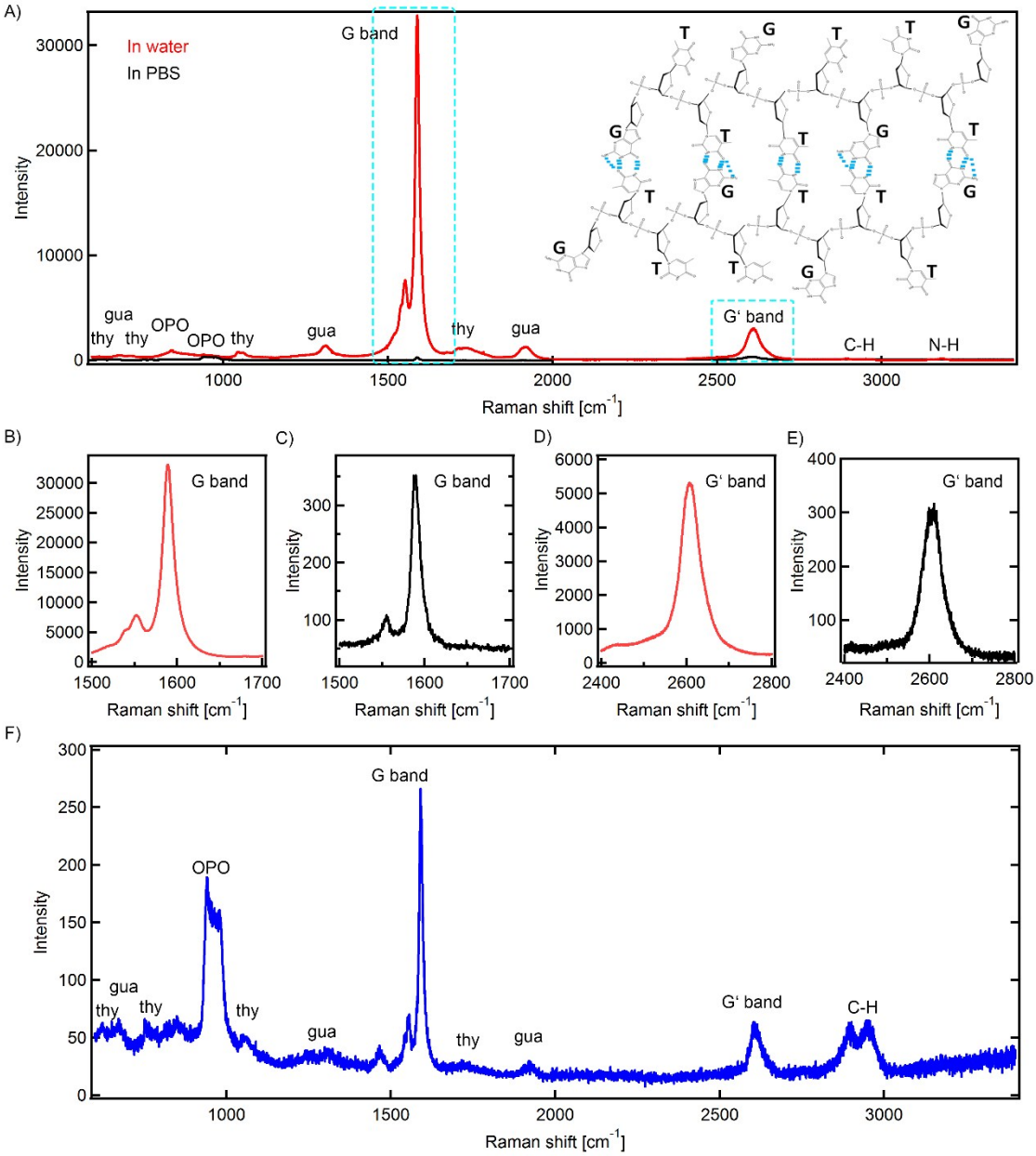

Fig. S5 (A) Raman spectra of ((GTT)3G)n/(7,6) CNT complexes formed in water (red trace) and PBS (black trace). (B) and (C) closer inspection of G band's vibrations at 1582 cm^{-1} for ssDNA/CNT complexes formed in pure water (B, red trace) and PBS (C, black trace) (the assignments of every peak can be found in Table S1). (D) and (E) Closer inspection of G' band's vibrations at 2610 cm^{-1}. (F) In-situ PBS induced change of Raman spectra. After collecting the Raman spectrum (Figure S5A, red trace), the same sample of $((GTT)_3G)n$/(7,6) CNT-ssDNA complexes formed in water were treated with PBS solution and used to record the Raman spectrum again. The great similarity of Raman spectrum in Figure S5A (red trace) and Figure S5F indicates the good reproducibility of the experiment as well as the reversibility of the tightening process.

SI-6 CD characterization on different ssDNA/CNT complexes

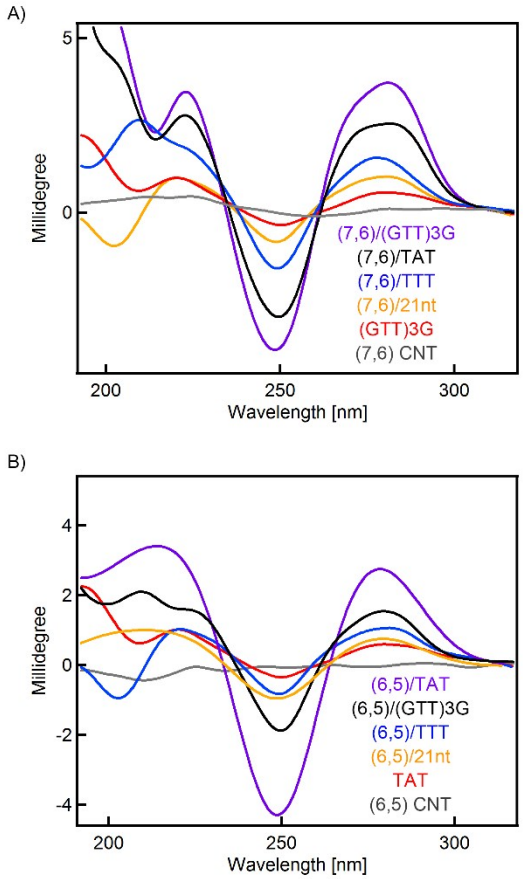

Fig. S6 CD spectra of two types of ssDNA/CNT complexes. (A) (7, 6) CNT (gray trace), ssDNA [((GTT)3G)n] (red trace), (7, 6) CNT/ 21nt (orange trace), (7, 6) CNT/ TTT (blue trace), (7, 6) CNT/ (TAT)n (black trace) and (7, 6) CNT/ ((GTT)3G)n (purple trace); (B) (6, 5) CNT (gray trace), ssDNA--(TAT)n (red trace), (6, 5) CNT/ 21nt (orange trace), (6, 5) CNT/ TTT (blue trace), (6, 5) CNT/ ((GTT)3G)n (black trace) and (6, 5) CNT/(TAT)n (purple trace). "21nt" represents the RCA product of a random sequence (Primer: CCGCTTCTGTCCACGAATCAG, template: GGCGAAGACAGGTGCTTAGTC). TTT represents poly T.

SI-7 CD characterization of ((GTT)3G)n/ (7, 6) CNT in the presence of PBS

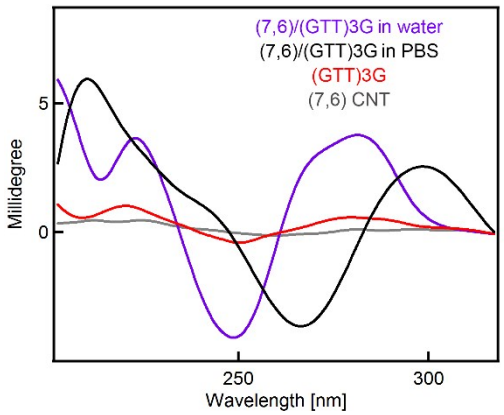

Fig S7 CD spectra of (7, 6) CNT (grey trace), ssDNA--((GTT)3G)n (red trace), (7, 6) CNT/ ((GTT)3G)n complexes in water (purple trace) and in PBS (black trace), respectively.

SI-8 The effects of stretching length, relaxation, waiting time on the complexes in water

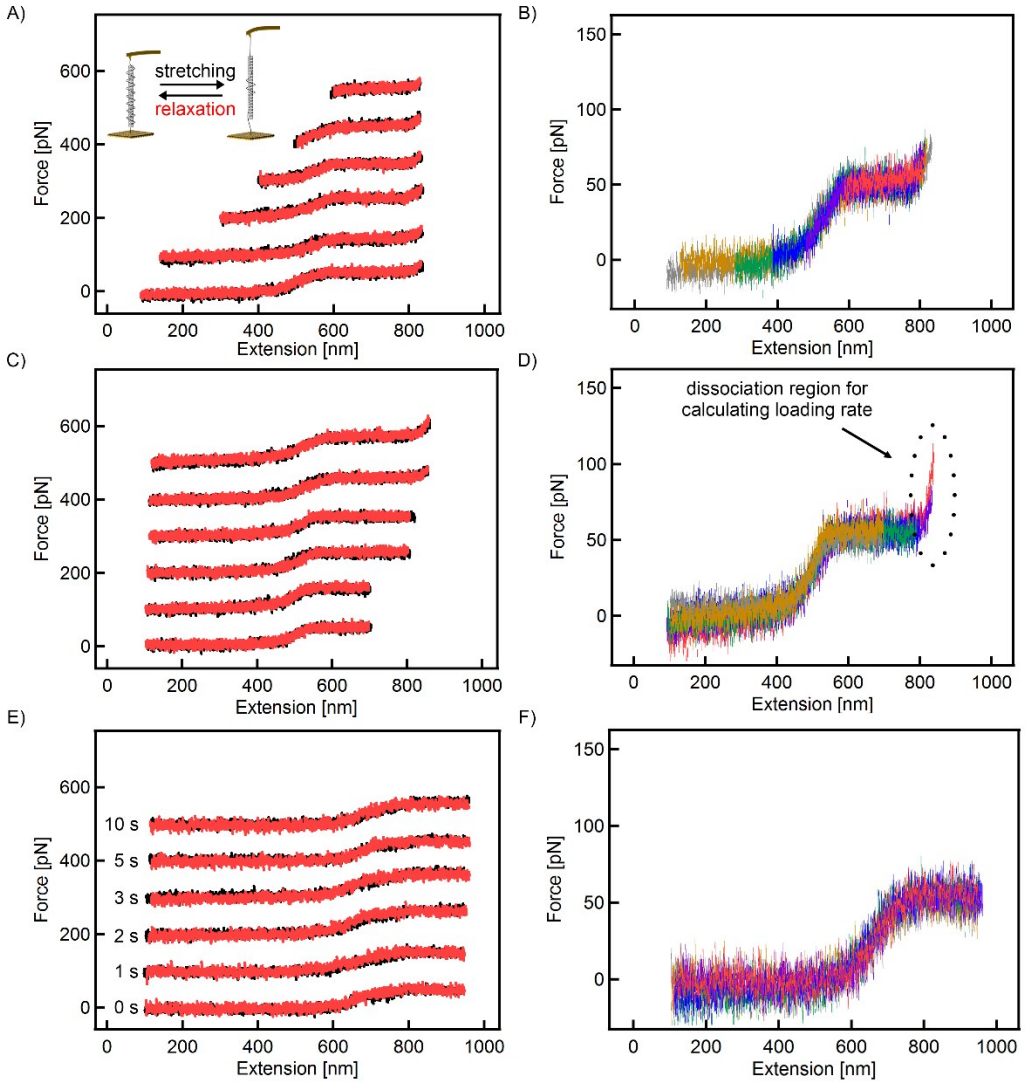

Fig S8 The effects of chain conformation, stretching length, waiting time on the unbinding-rebinding processes of ssDNA-CNT complexes in water. First, the complexes were stretched to partially break the binding sites between ssDNA and CNT within the complexes while avoiding detachment of the DNA molecule from either the AFM tip or the gold substrate. Then the molecule was relaxed to a position ~ 100 nm away from the surface and stayed there for 2 s (except for E and F) to allow the reformation of ssDNA-CNT complexes. Then the ssDNA molecule was stretched again. (A) Typical F-E curve after relaxing the same molecule to different starting extensions (Inset: The scheme of the stretching-relaxation SMFS experiment). (C) Effect of stretching length on the unbinding/rebinding of ssDNA from/to CNT. (E) Effect of waiting time on the reformation of ssDNA-CNT complexes. (B), (D) and (F) show the superposition of the stretching curves shown in (A), (C) and (E), respectively. The loading rate was obtained by multiplying the retract velocity by apparent elasticity of the molecular bridge, which was determined from the slope of the curves on the last several data points before the dissociation events (as marked in Figure D).

SI-9 Force clamp spectroscopy monitors the folding trajectory of ssDNA/CNT in PBS

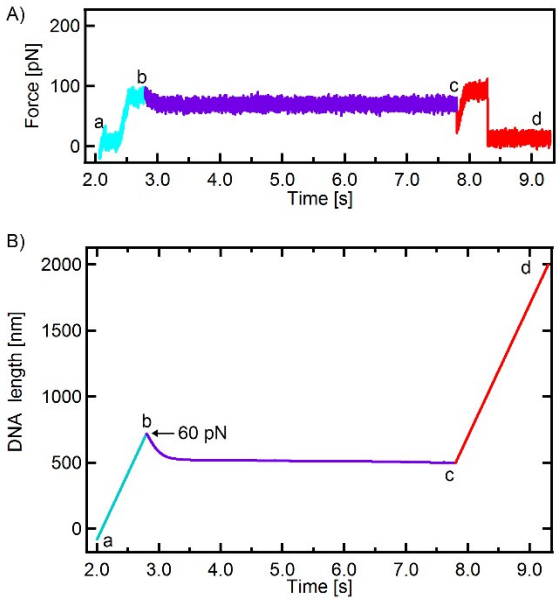

Fig. S9 (A) Change of force with time. The experimental set-up, after approaching and being brought into contact with the surface of the substrate incubated with ((GTT)3G)n/ (7, 6) complex, the cantilever was allowed to retract for a while so that the shoulder plateau (80 pN) in Force-Extension channel appeared marking that ssDNA chain was unbound from the tube (from a to b). A clamp force at 60 pN was loaded on the cantilever for 5 s, the DNA chain spontaneously contract (from b to c). To further confirm that the ssDNA had rebound to the tube, after clamped for 5 s, the cantilever was retracted and we observed the shoulder plateau (80 pN) appeared again (from c to d). (B) Changes in the length of a single DNA chain in response to the stretching force. Stretching the ssDNA chain at constant speed causes a series of unfolding events (from a to b). A clamp force at 60 pN was loaded on the cantilever for 5 s, the DNA chain spontaneously contract with several stages marking the folding events of ssDNA on CNT (from b to c). The refolded structure was confirmed by unbinding ssDNA chain from CNT again in a constant speed mode (from c to d).

SI-10 SMFS on (TAT)n/ (6, 5) CNT

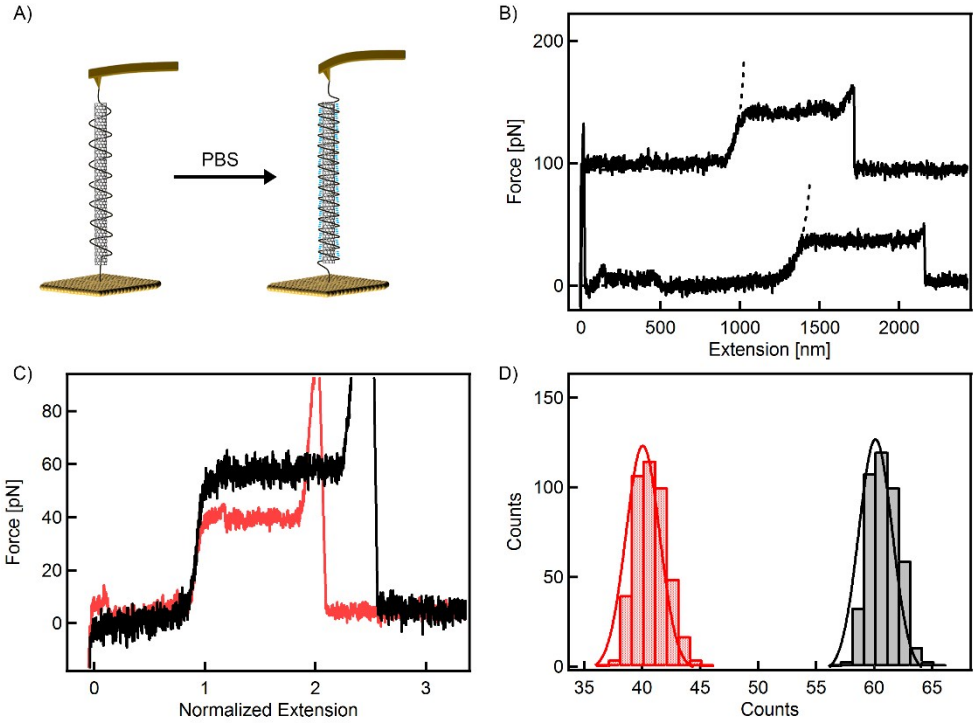

Fig. S10 (A) Schematic of SMFS on (TAT)n/ (6, 5) CNT. (B) Typical force-extension curves of (TAT)n/ (6, 5) CNT in water. The dash lines represent the WLC fits (with persistence length of 2.5 nm). (C) Comparison of typical F-E curves of (TAT)n/ (6, 5) CNT obtained in water (trace in red) and PBS (trace in black). (D) Force distribution of (TAT)n/ (6, 5) CNT obtained in water (trace in red), in PBS (trace in black).

Tab. S1 Summary of the Raman peaks obtained on ((GTT)3G)n/(7,6) CNT complexes and their assignments

In water (cm^{-1})	In PBS(cm^{-1})	Assignment
620	620	thy
680	670	gua
730		thy
845	825	OPO
950	950	OPO
1315	1305	gua
1558	1560	gua
1595	1590	G band (CNT)
1685	1650	thy, gua (C=O)
1710	1710	gua (C=O)
2860	2900	G' band (CNT)
2885	2950	C-H
3140		N-H
3170		N-H