Supplementary Material (ESI) for Chemical Communications

Supporting Information

For

Construction, DNA Wrapping and Cleavage of A Carbon Nanotube-Polypseudorotaxane Conjugate

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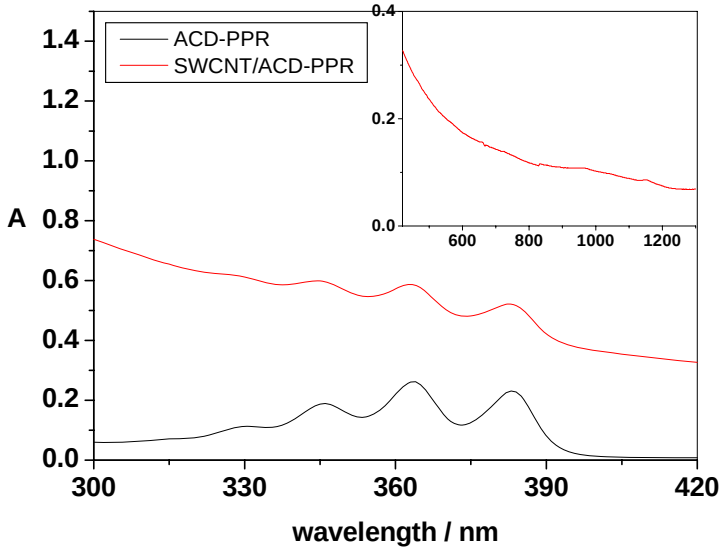
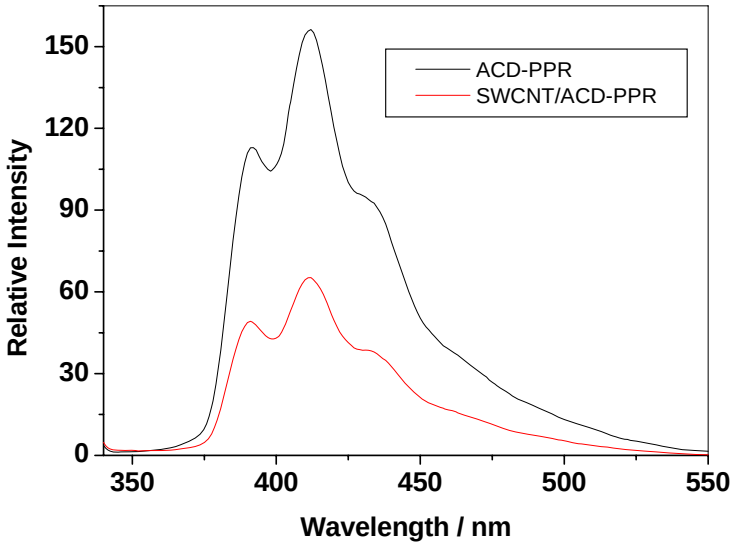
Materials and Methods

General. SWCNTs were obtained from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences. Calf thymus DNA was commercially available and treated according to the reported method.[1] Plasmid DNA pEGFP-C2 (4.7kb) was purified from *E. coli* DH5α using Wizard Plasmid DNA Purification System. The concentration of plasmid DNA was measured through UV-vis spectrophotometric analysis. Circular dichroism and UV-vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a JASCO J-715S spectropolarimeter or a Shimadzu UV-2401PC spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25°C. Fluorescence spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) on a JASCO FP-750 fluorescence spectrometer equipped with a PTC-348WI temperature controller and the excitation and emission slits are both 5 nm width. Transmission electron microscopy (TEM) experiments were performed on a Philips Tacnai G^2 20 S-TWIN microscope operating at 200 kV. Atomic force microscope (AFM) experiments were performed on a multi mode IIIa AFM.

Preparation of SWCNT/ACD-PPR Conjugate. To the mixture of SWCNTs (20 mg) and ACD-PPR (20 mg) was added several drops of the mixed solution of ethanol and water. The mixture was ground for 30 minutes by using an agate mortar and pestle and placing for an hour. This procedure was repeated three times. The resultant mixture was suspended in 10 mL of water and sonicated for 2 hours. The unreacted SWCNT was removed by centrifugation, and the supernatant was dialyzed (MWCO of dialysis membrane 25000) against deionized water until no fluorescent signal could be detected in the dialyzate to remove free ACD-PPR. The solution was evaporated under the reduced pressure to dryness to give the SWCNT/ACD-PPR conjugate (23.1 mg, yield 58%) as a black solid. After collection by centrifugation, the unreacted SWCNT was weighed to be 11.0 mg. This means that the content of SWCNT in the SWCNT/ACD-PPR complex was 9.0 mg, and the ratio of ACD-PPR to SWCNT (w/w) in the conjugate was ca. 61: 39. The water solubility of SWCNT/ACD-PPR conjugate was measured to be ca. 2.5 $mg \cdot mL^{-1}$.



(a)



(b)

Figure S1. (a) UV-vis spectrum of ACD-PPR and SWCNT/ACD-PPR conjugate (10 μM calculated by anthryl unit); (b) Fluorescence spectra of ACD-PPR and SWCNT/ACD-PPR conjugate (1 μM calculated by anthryl unit). Excitation wavelength: 330 nm.

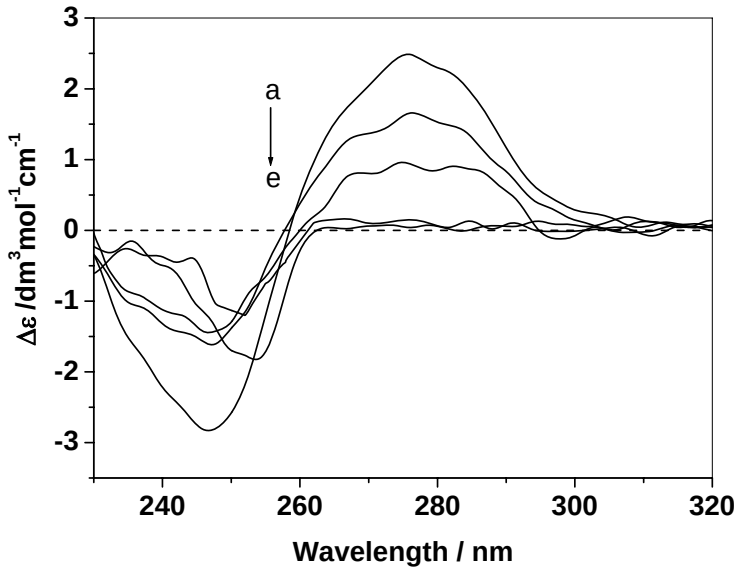


Figure S2. Circular dichroism spectra of ct-DNA (2.8×10^{-5} mol·dm^{-3}) with the addition of SWCNT/ACD-PPR conjugate in phosphate buffer solution (pH 7.2) at 25°C. The concentration of SWCNT/ACD-PPR conjugate was 0, 1.5, 3.0, 6.0, 9.0×10^{-4} mol·dm^{-3} from a to e.

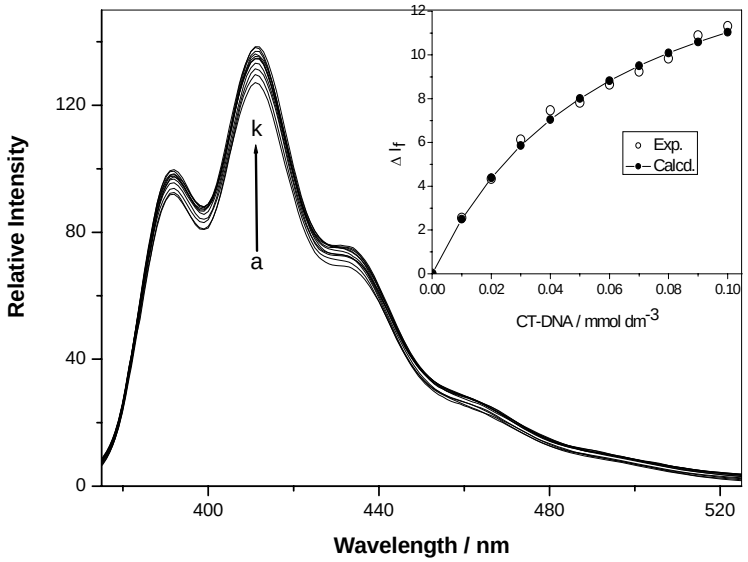


Figure S3. Fluorescence spectra of SWCNT/ACD-PPR conjugate (2.0×10^{-6} mol·dm^{-3} calculated by anthryl-modified β-cyclodextrin inclusion unit) with the addition of ct-DNA ($0 \sim 1.0 \times 10^{-4}$ mol·dm^{-3} from a to k) in phosphate buffer aqueous solution (pH 7.2) at 25°C. Inset: the curve-fitting analysis of the differential intensity (ΔI_f) to calculate the binding constant. (λ_{ex} = 330 nm, λ_{em} = 411 nm).

In the previous section, we demonstrated that the ratio of ACD-PPR to SWCNT (w/w) in the

SWCNT/ACD-PPR conjugate was ca. 61:39. Using this ratio we could calculate the content of ACD-PPR in the conjugate. Moreover, an ACD-PPR could be divided to 9 anthryl-modified β-cyclodextrin inclusion units.[1] Therefore, the effective binding constant of every anthryl-modified β-cyclodextrin inclusion unit in the SWCNT/ACD-PPR conjugate could be calculated through a nonlinear least-squares curve-fitting method[2] (equation (1)) by analyzing the sequential changes of fluorescence intensity (ΔF) of SWCNT/ACD-PPR conjugate at 411 nm that occurred with changes in the DNA concentration.

$$\Delta F = \frac{\alpha([\mathrm{H}]_0 + [\mathrm{G}]_0 + 1/\mathrm{Ks}) \pm \sqrt{\alpha^2([\mathrm{H}]_0 + [\mathrm{G}]_0 + 1/\mathrm{Ks})^2 - 4\alpha^2[\mathrm{H}]_0[\mathrm{G}]_0}}{2} \qquad (1)$$

In this equation, $[\mathrm{H}]_0$ and $[\mathrm{G}]_0$ were the initial concentration of host (anthryl-modified β-cyclodextrin inclusion unit in the SWCNT/ACD-PPR conjugate) and guest (DNA) respectively, while ΔF was the fluorescence spectral changes of host upon addition of guest, where $\Delta F = F$ (with guest) - F (without guest) was assumed to be proportional to the concentration of product, *i.e.* $\Delta F = \alpha[\mathrm{H{\cdot}G}]$. The proportionality coefficient α was taken as a sensitivity factor for the fluorescence change.

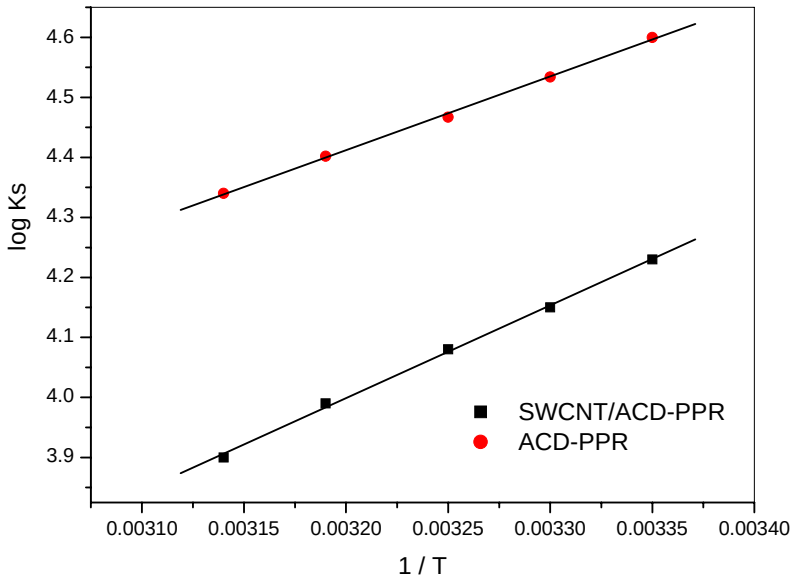


Figure S4. Plot of log*K*s versus 1/T for the binding of ACD-PPR and SWCNT/ACD-PPR with ct-DNA.

For Figure S4, there were two equations,

$$\Delta G° = -RT\ln Ks \qquad (2)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

From these equations, we could get the van't Hoff equation,

$$\log Ks = (1/2.303R)(\Delta S° - \Delta H°/T)$$

Then, we selected 5 different temperatures (T=298.15, 303.15, 308.15, 312.15, 317.15 K) to run fluorescent titrations and calculated the corresponding *K*s values. By using the van't Hoff equation, we can obtain the $\Delta H°$ and $T\Delta S°$ as shown in Table S1.

Table S1. Thermodynamic parameters for the binding of ACD-PPR and SWCNT/ACD-PPR with ct-DNA in phosphate buffer aqueous solution (pH 7.2) at 25°C.

	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}
SWCNT/ACD-PPR+ct-DNA	24.2	29.6	-5.4
ACD-PPR+ct-DNA	26.3	23.6	2.7

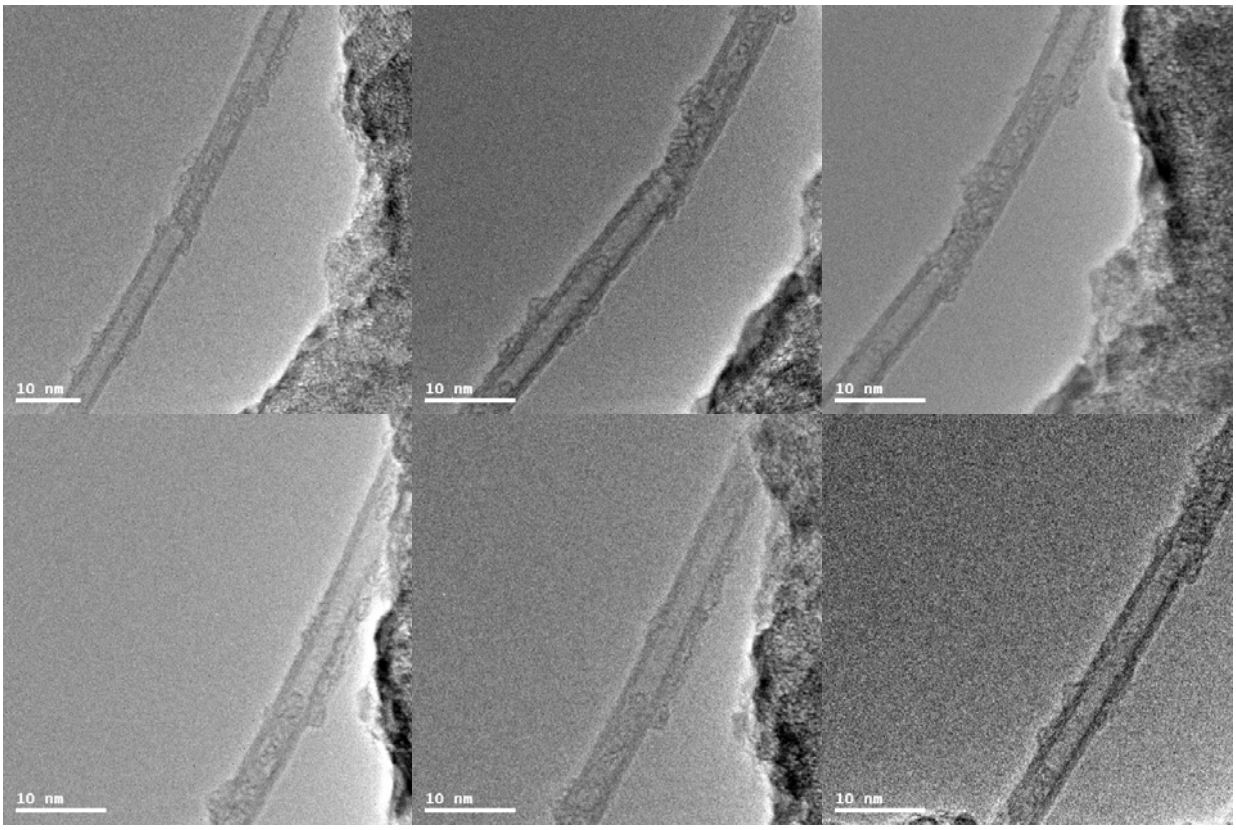


Figure S5. High-resolution TEM images of SWCNT/ACD-PPR .

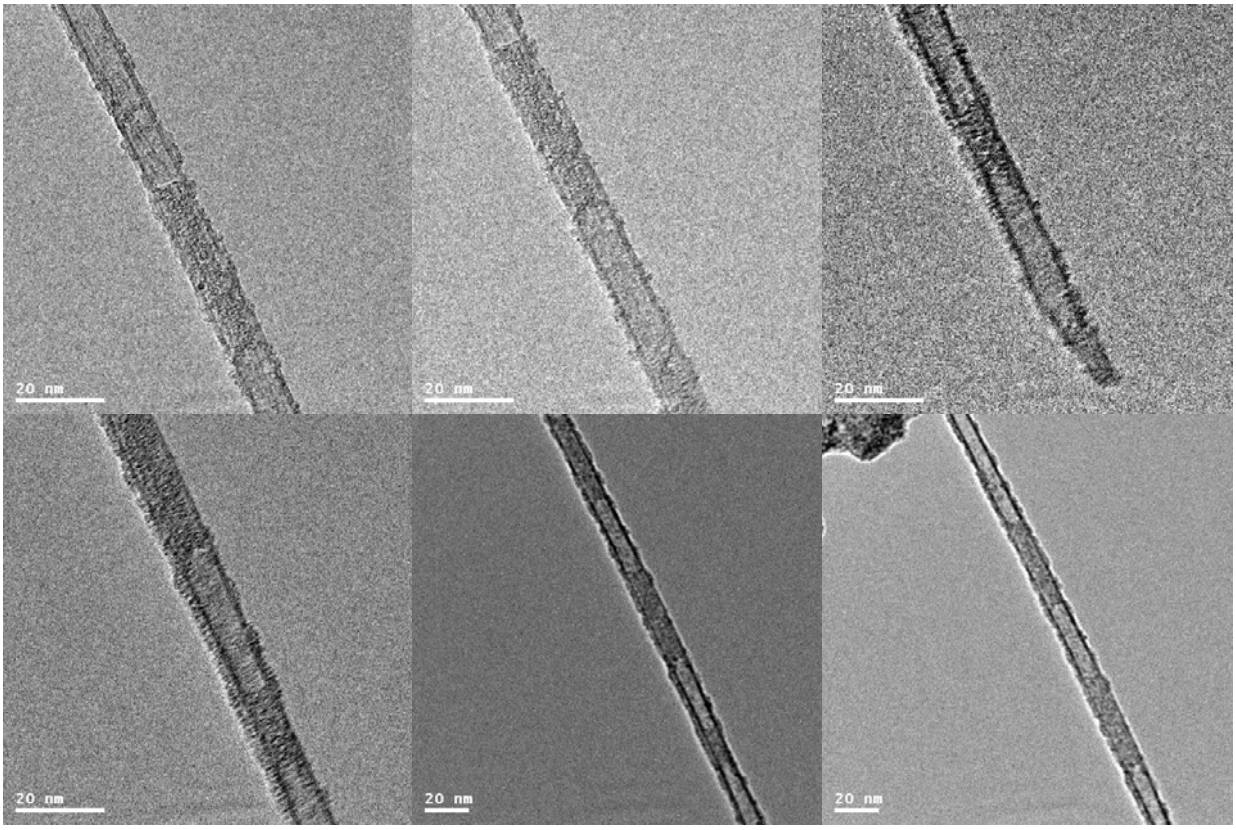


Figure S6. High-resolution TEM images of DNA/ SWCNT/ACD-PPR.

References

1. Liu, Y.; Yu, L.; Chen, Y.; Zhao, Y.-L.; Yang, H. *J. Am. Chem. Soc.* **2007**, *129*, 10656-10657.

2. Liu, Y.; Han, B.-H.; Zhang, H.-Y. *Curr. Org. Chem.*, **2004**, *8*, 35-46