Supporting Information for

Binding Affinities and Thermodynamics of Noncovalent Functionalization of Carbon Nanotubes with Surfactants

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Derivation of Hill equation using equilibrium constant

The transition during cosurfactant replacement is sigmoidal in nature and can be described by the Hill equation.[S1-3] Since we did not observe any change of FMN absorption during titration (Fig. S5), we assume that FMN and other surfactant is not interacting. Therefore the equilibrium reaction can be considered as

$$\text{FMN-SWNT + cosurfactant} \xrightleftharpoons{K_{FMN\text{-}cosurfactant}} \text{cosurfactant-SWNT + FMN} \cdots\cdots\cdots \text{(S1)}$$

where $K_{FMN-cosurfactant}$ is an equilibrium constant of exchange from FMN-SWNT to cosurfactant-SWNT, The equilibrium constant of the above reaction can be rearranged as

$$K_{FMN-cosurfactant} = \frac{[cosurfactant-SWNT][FMN]}{[FMN-SWNT][cosurfactant]} \cdots\cdots\cdots\cdots\cdots\cdots \text{(S2)}$$

Now, we consider the total binding sites. According to the previous equation[1-3],

$$\rho = \frac{Binding\ sites\ occupied}{Total\ binding\ sites} = \frac{[cosurfactnat-SWNT]}{[FMN-SWNT]+[cosurfactant-SWNT]} \cdots\cdots\cdots\cdots\cdots \text{(S3)}$$

where ρ is fluorescence intensity of cosurfactant-SWNT.

Rearranging Eqn. (S2) in terms of [cosurfactant-SWNT] and substituting it into Eqn. (S3) gives

$$\rho = \frac{\frac{K_{FMN-cosurfactant} \cdot [FMN-SWNT] \cdot [cosurfactant]}{[FMN]}}{[FMN-SWNT] + [\frac{K_{FMN-cosurfactant} \cdot [FMN-SWNT] \cdot [cosurfactant]}{[FMN]}]}$$

$$= \frac{K_{FMN-cosurfactant} \cdot [cosurfactant]}{[FMN] + K_{FMN-cosurfactant} \cdot [cosurfactant]}$$

$$= \frac{[cosurfactant]}{\frac{[FMN]}{K_{FMN-cosurfactant}} + [cosurfactant]} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(S4)}$$

Generalizing Eqn. (S1) for equilibrium reaction with reaction coefficients can be written as

$$\text{FMN-SWNT + } \gamma \text{ cosurfactant} \xrightleftharpoons{K_{FMN\text{-}cosurfactant}} \text{cosurfactant-SWNT + } \delta \text{ FMN} \cdots\cdots \text{(S5)}$$

where γ and δ are coefficients of surfactants. Likewise Equation S4, one can express ρ in terms of concentration as follows.

$$\rho = \frac{[cosurfactant]^{\gamma}}{[\frac{[FMN]^{\delta}}{K_{FMN-cosurfactant}}]^{\gamma} + [cosurfactant]^{\gamma}} \quad \text{(S6)}$$

By assuming that δ simply depends on γ, one can reduce complexity of the above equation as follows.

$$\rho = \frac{[cosurfactant]^{\gamma}}{[\frac{[FMN]}{K_{FMN-cosurfactant}}]^{\gamma} + [cosurfactant]^{\gamma}} \quad \text{(S7)}$$

here [FMN] / $K_{FMN\text{-}cosurfactant}$ is equal to [cosurfactant]$^{\gamma}$ at which half of the SWNTs are bound. For the calculation of equilibrium constant and Hill coefficient, the concentration of FMN was set to 2.09 mM, the initial concentration of FMN-SWNT dispersion.

FMN interaction with other surfactants

In order for the above equilibrium reaction to hold, FMN and other surfactants should have no interaction. For this, we measured absorption spectra of FMN in the absence and presence of SDBS, SC, and SDS. We titrated FMN solution with increasing amount of SDBS, SC, and SDS. The results are shown in Fig. S5, where the initial FMN absorption spectra peaking at 370 and 445 nm was not changed after addition of cosurfactants. Zoom-in spectra in inset showed no change in absorption maximum.

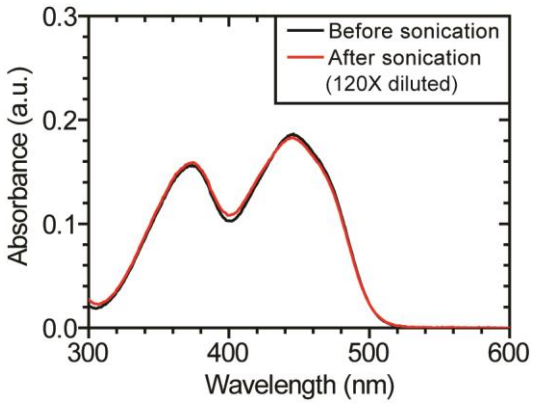

Figure S1. Absorption spectra of FMN without SWNTs before and after probe-sonication. The solution was obtained using same amount of FMN in water and was treated with same protocol for FMN-SWNTs. In order to adjust to the absorbance limit (*i.e.* 3), we opt to dilute the sample by 120 times

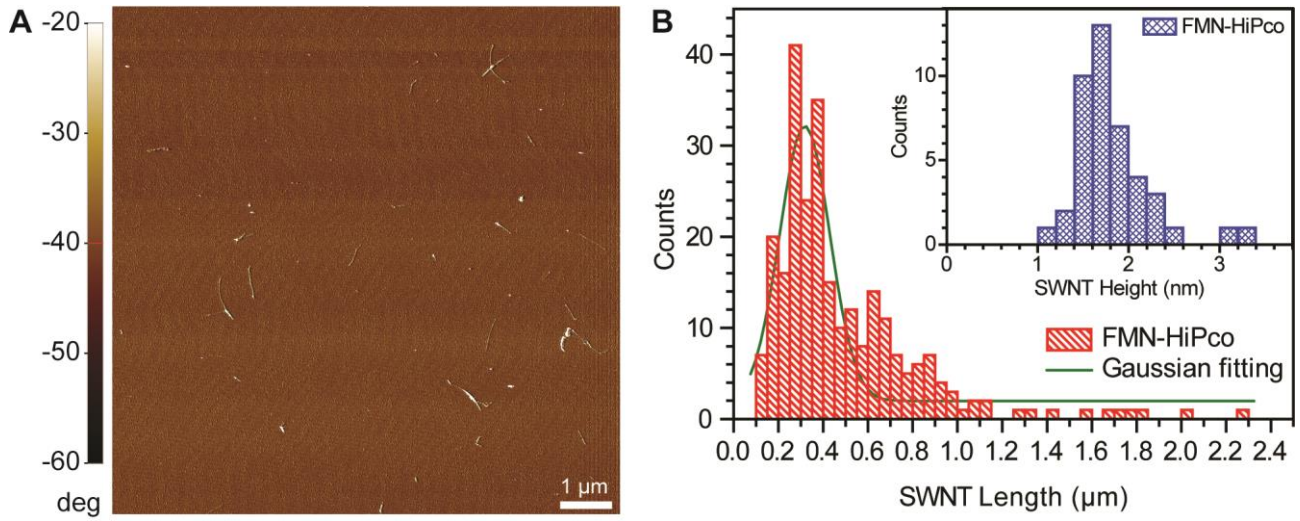

Figure S2. Representative atomic force microscopy (AFM) phase image and the corresponding length and height histograms of dispersed nanotubes. Phase images of (A) FMN-wrapped SWNTs and (B) corresponding length histogram. Green curves represent Gaussian fitting of the length distributions of FMN-wrapped SWNTs. Inset of (B) display the height distribution profile of FMN-wrapped SWNTs.

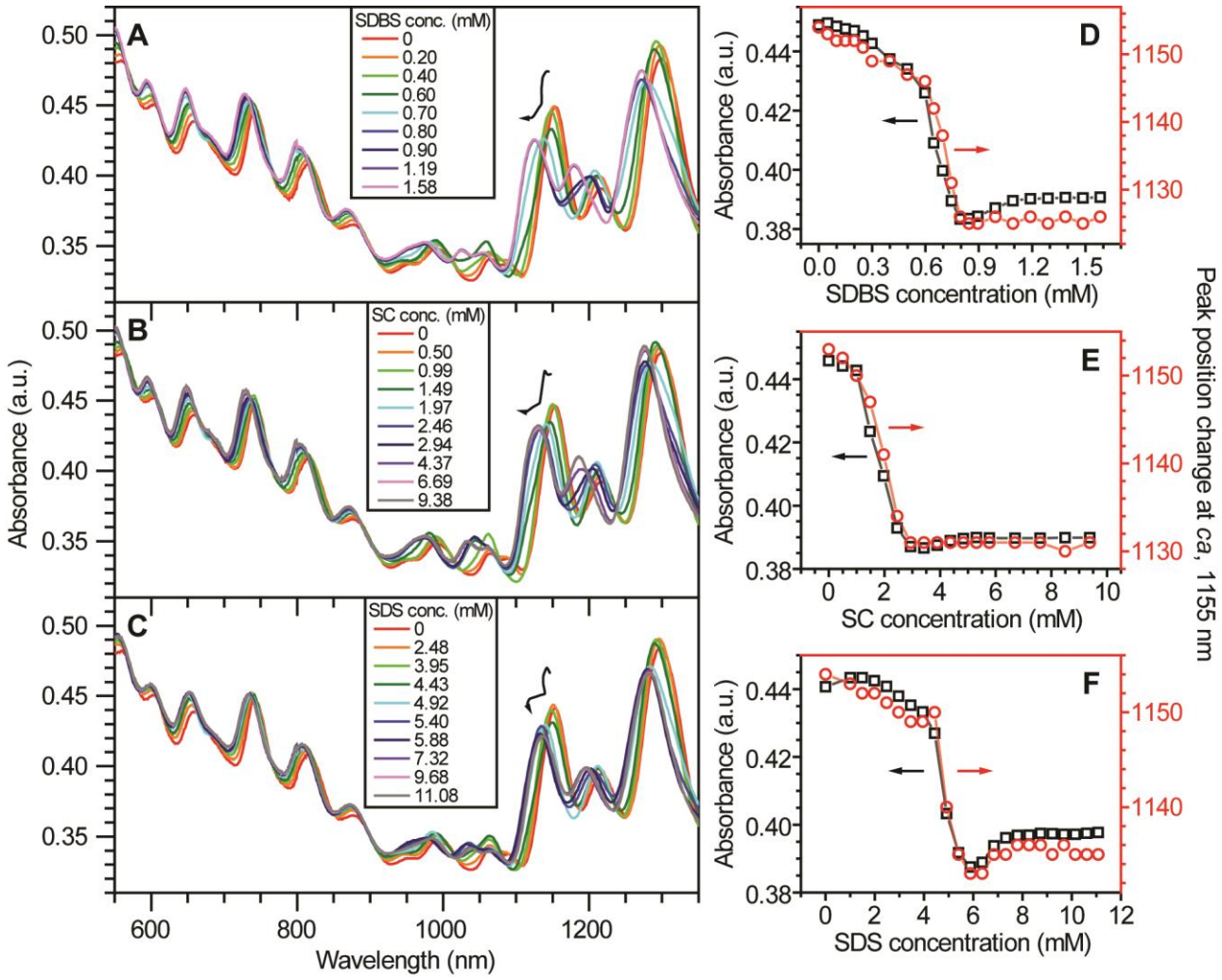

Figure S3. Absorption spectra of FMN-wrapped SWNTs titrated with (A) SDBS, (B) SC, and (C) SDS. (D-F) illustrate absorption intensity change (black trace) and 1,155 nm band position change (red trace), which corresponds to a composite of (9,4), (7,6), and (8,4) nanotubes.

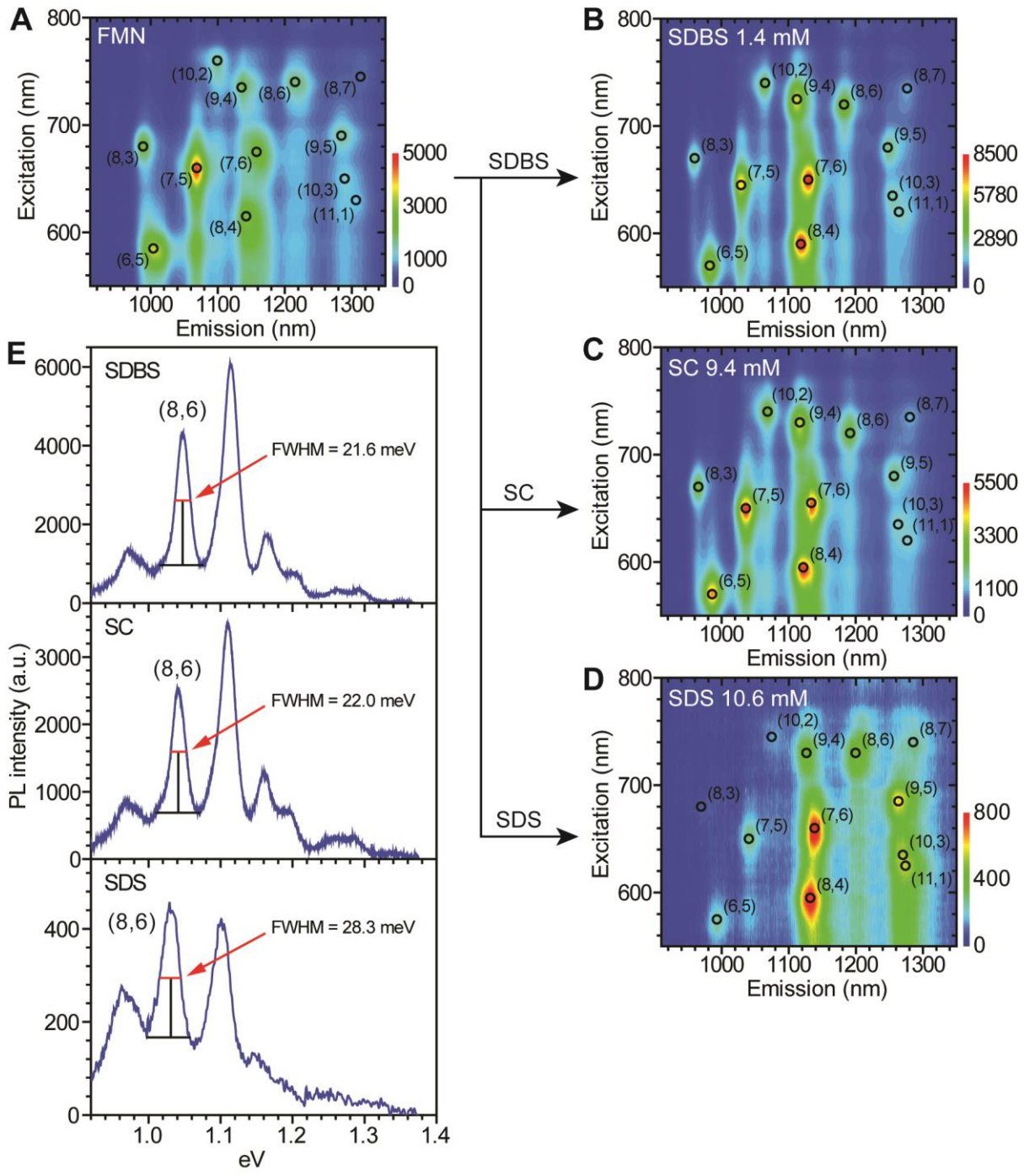

Figure S4. PLE maps of (A) initial FMN-wrapped SWNTs and the corresponding replaced dispersion of (B) SDBS-replaced, (C) SC-replaced, and (D) SDS-replaced nanotube dispersions. (E) FWHM of PL from (8,6) nanotubes for SDBS- (top), SC- (middle), and SDS- (bottom) replaced position.

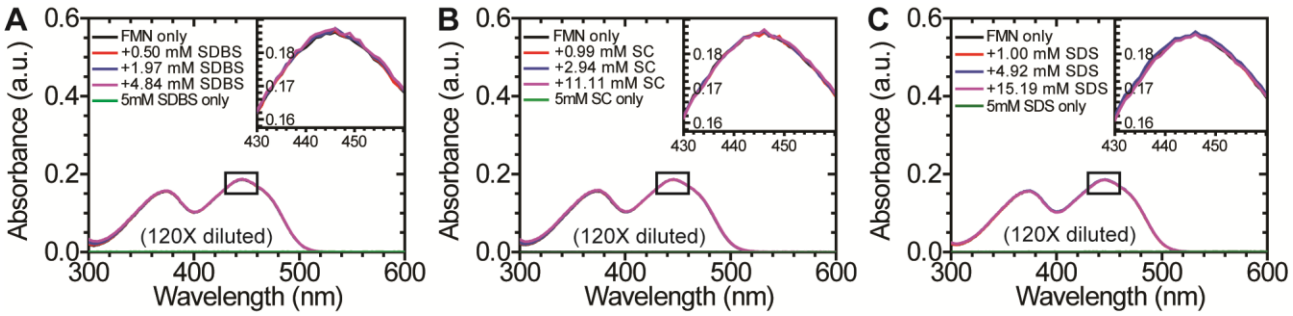

Figure S5. Absorption spectra of FMN titrated with (A) SDBS, (B) SC, and (C) SDS. Insets are scaled-up absorbance image from 430 nm to 460 nm. After titration of solution containing 2.09 mM FMN, the titrated solution along with the initial FMN one was diluted by 120 times.

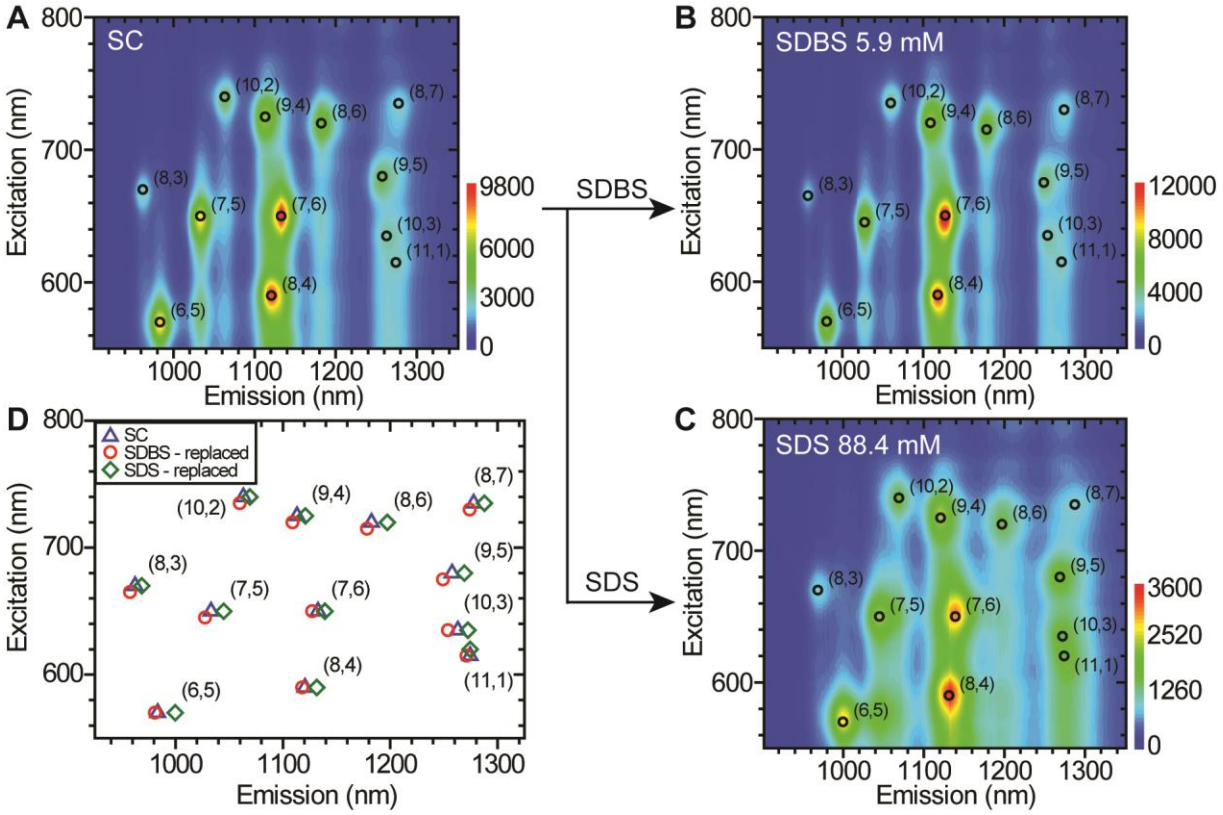

Figure S6. PLE maps of (A) the initial SC-wrapped SWNTs, the corresponding titrated dispersion of (B) SDBS-replaced, and (C) SDS-replaced nanotube dispersions. (D) illustrates the final PL position of various surfactant-wrapped SWNTs with respect to the SC-wrapped SWNT (indicated by a triangle).

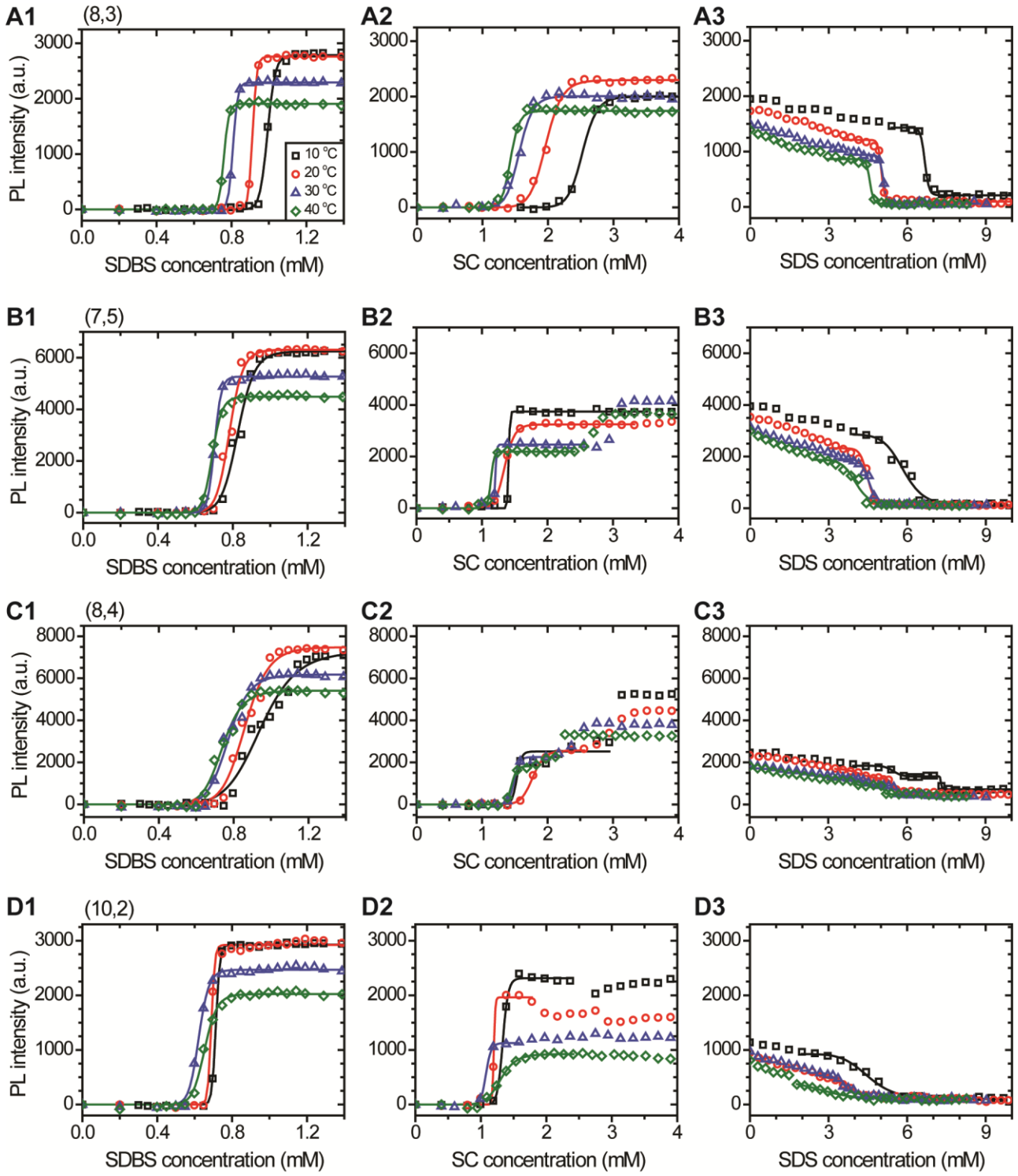

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Figure S7. Temperature-dependent transition change of 11 other chiral nanotubes, except the (6,5) tube listed in Figure 6. (A1-K1) FMN to SDBS replacement. (A2-K2) FMN to SC replacement, and (A3-K3) FMN to SDS replacement. (10 ℃: black square, 20 ℃: red circle, 30 ℃: blue triangle, 40 ℃: green diamond).

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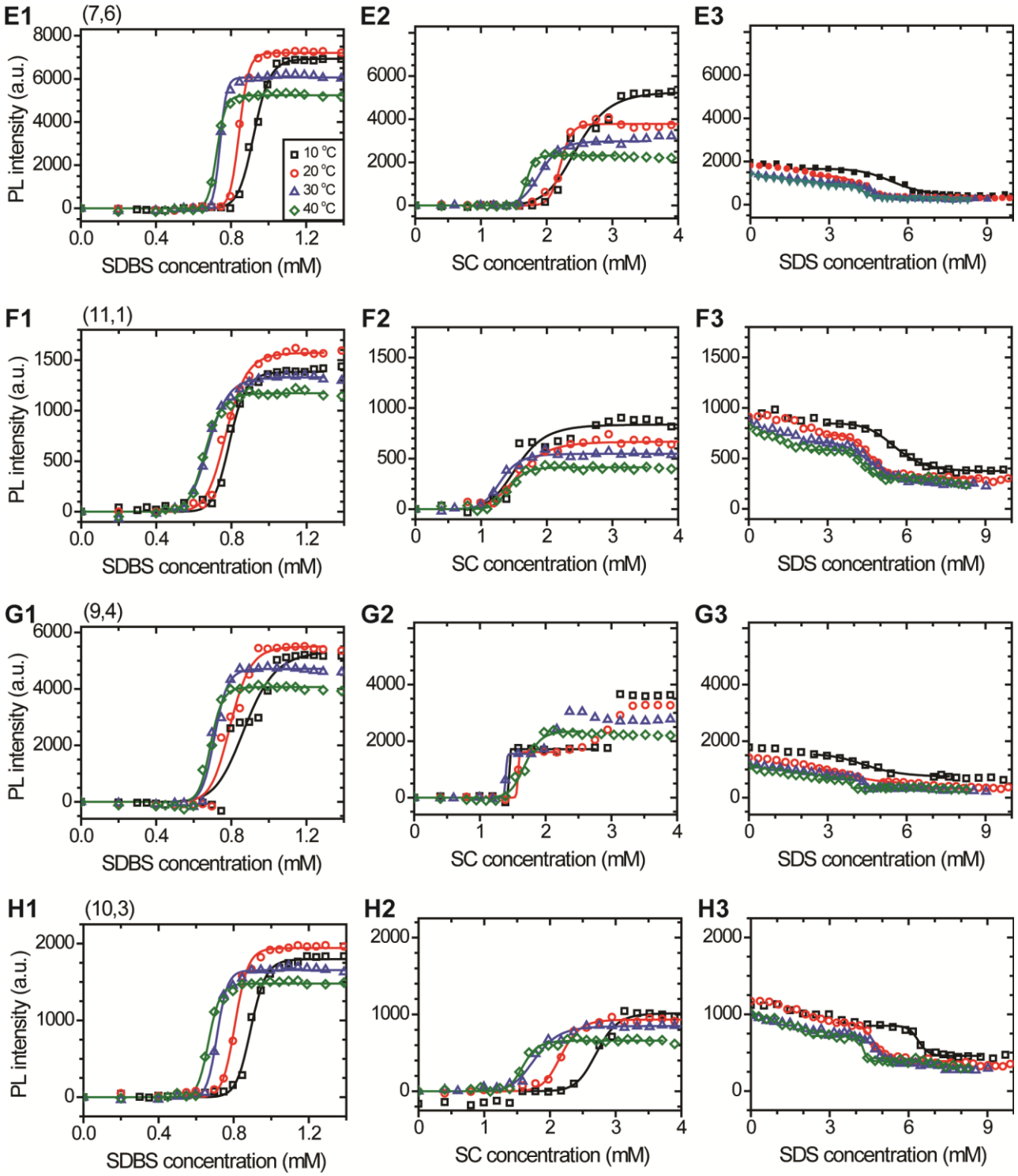

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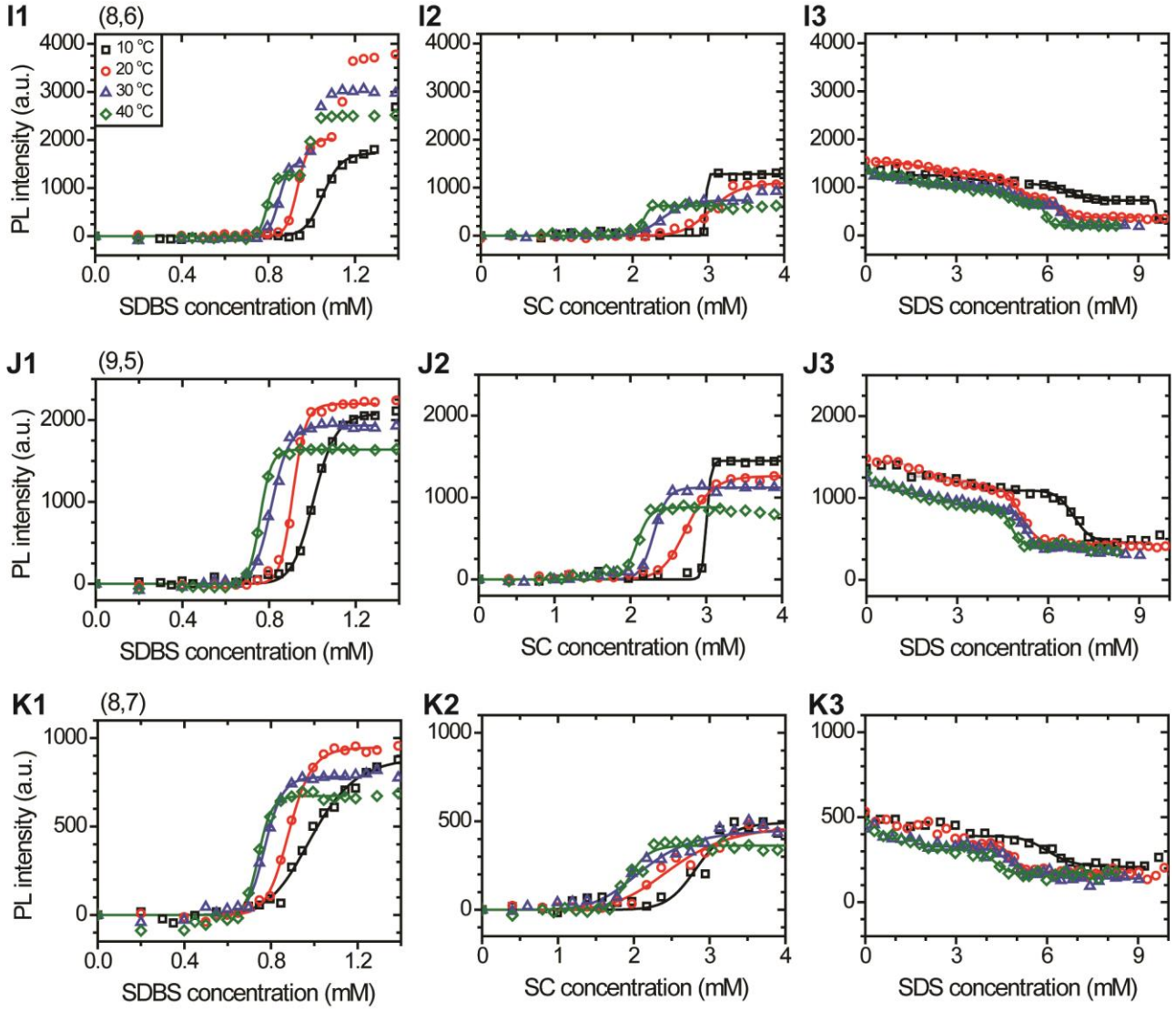

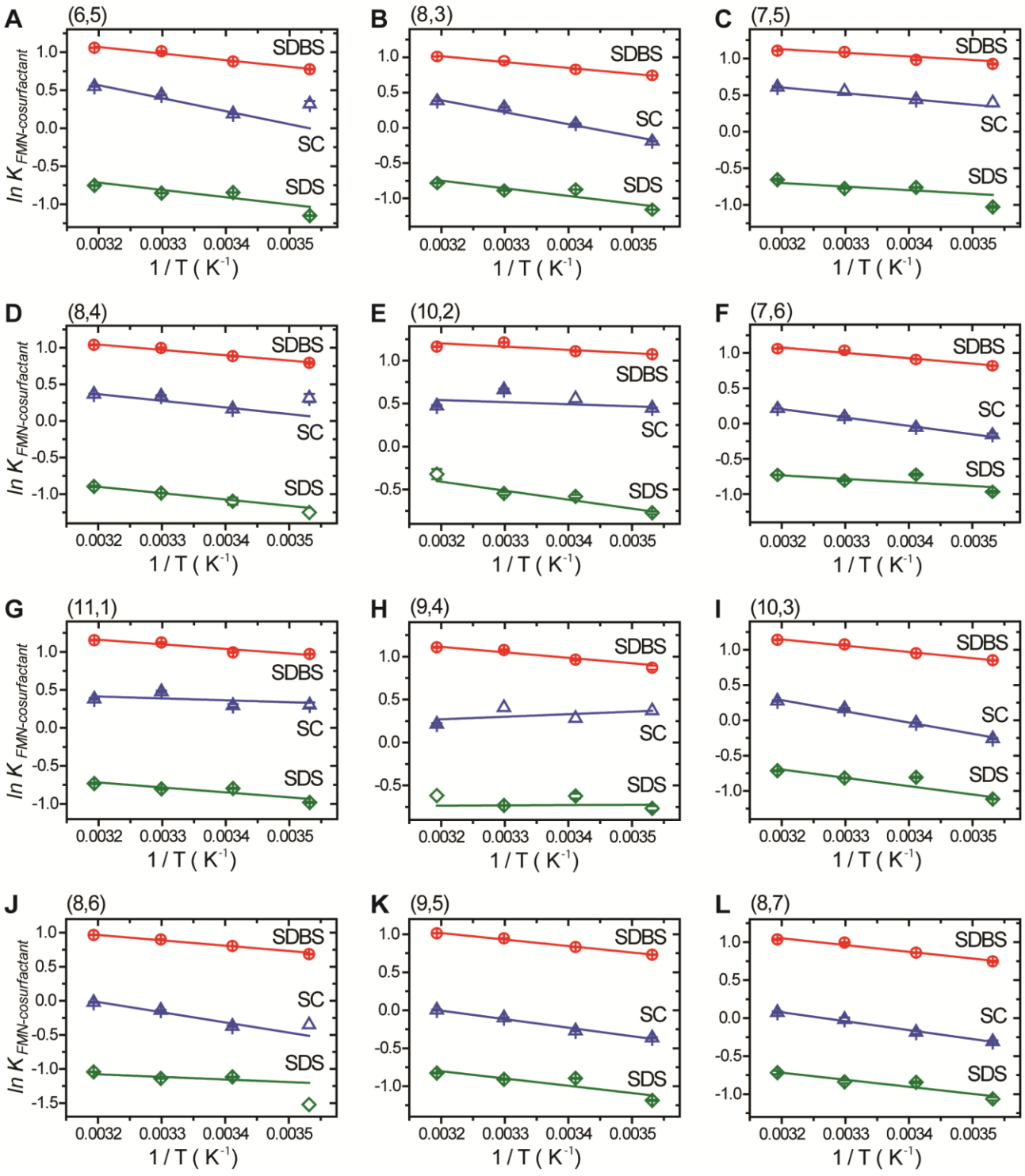

Figure S8. Plot between the natural logarithmic equilibrium constant *K* and 1/*T* (see main text). (FMN-wrapped nanotube with SDBS: red circle, SC-replacement: blue triangle, and SDS-replacement: green diamond). The straight line is the linear regression fit of ln*K* values at four different temperatures (313, 303, 293, and 283 Kelvin from left to right of x axis).

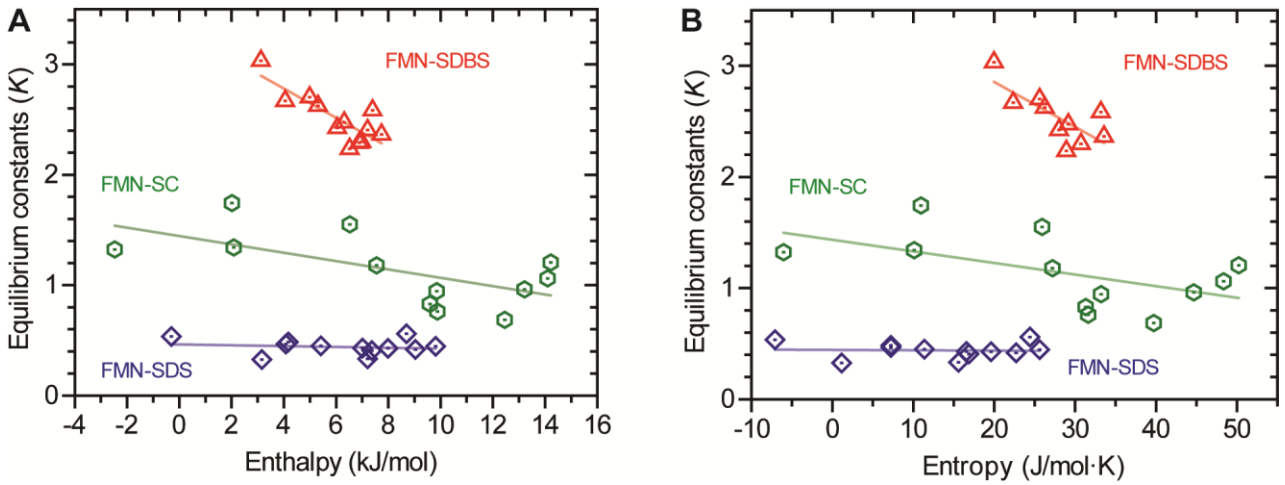

Figure S9. Relationship between the equilibrium constant (*K*) and thermodynamic parameters of (A) enthalpy change (Δ*H*) and (B) entropy change (Δ*S*) according to the surfactant exchange system (FMN-SDBS: red triangle, FMN-SC: green hexagon, FMN-SDS: blue diamond). The symbols indicate nanotube chirality (Table S2). The linear regression fit (solid lines) was drawn to guide the trends and magnitude of each surfactant replacement.

Table S1. Temperature- and chirality-dependent equilibrium constant (K) and Hill coefficient (γ).

(A) FMN to SDBS replacement on SWNTs.

Assignment (n,m)	Diameter [nm]	10 °C		20 °C		30 °C		40 °C	
		$K_{FMN\text{-}SDBS}$	γ	$K_{FMN\text{-}SDBS}$	γ	$K_{FMN\text{-}SDBS}$	γ	$K_{FMN\text{-}SDBS}$	γ
(6,5)	0.76	2.17±0.01	19.1±1.5	2.41±0.01	24.0±2.3	2.75±0.01	26.9±2.7	2.88±0.01	32.5±3.3
(8,3)	0.78	2.11±0.00	48.8±3.7	2.29±0.00	81.7±3.7	2.59±0.00	64.4±3.1	2.75±0.00	58.1±2.7
(7,5)	0.83	2.53±0.01	18.8±1.9	2.67±0.01	22.2±2.3	2.98±0.00	39.1±2.3	3.02±0.01	27.0±1.6
(8,4)	0.84	2.21±0.03	9.9±1.2	2.42±0.02	13.9±1.4	2.71±0.03	13.8±1.6	2.83±0.02	13.9±1.3
(10,2)	0.88	2.93±0.00	69.7±3.3	3.03±0.02	76.4[§]	3.36±0.01	23.5±1.7	3.20±0.01	19.9±1.4
(7,6)	0.89	2.27±0.01	21.9±1.4	2.47±0.00	33.9±2.0	2.82±0.01	43.9±5.0	2.89±0.01	31.8±1.9
(11,1)	0.92	2.64±0.02	18.4±1.7	2.70±0.02	14.3±1.1	3.08±0.01	13.0±0.7	3.17±0.02	14.8±1.0
(9,4)	0.92	2.39±0.06	10.8±2.4	2.62±0.03	15.0±2.3	2.93±0.02	21.1±3.1	3.03±0.02	22.2±2.7
(10,3)	0.94	2.34±0.01	22.5±1.8	2.58±0.01	23.7±2.0	2.93±0.01	26.3±2.3	3.13±0.01	22.2±1.8
(8,6)	0.97	1.98±0.01	25.1±2.6	2.24±0.00	36.5±2.1	2.46±0.01	36.1±6.3	2.63±0.01	44.7±6.6
(9,5)	0.98	2.07±0.01	19.9±1.1	2.30±0.01	30.9±2.2	2.57±0.01	20.5±1.3	2.75±0.01	29.6±1.6
(8,7)	1.03	2.11±0.02	9.7±0.8	2.36±0.01	16.8±0.9	2.70±0.01	19.5±1.8	2.82±0.02	24.9±4.6
Average		2.31	24.5	2.51	28.4	2.82	29.0	2.92	28.5

(B) FMN to SC replacement on SWNTs.

Assignment (n,m)	Diameter [nm]	10 °C		20 °C		30 °C		40 °C	
		$K_{FMN\text{-}SC}$	γ	$K_{FMN\text{-}SC}$	γ	$K_{FMN\text{-}SC}$	γ	$K_{FMN\text{-}SC}$	γ
(6,5)	0.76	1.37±0.06	54.7[§]	1.21±0.00	12.0±0.4	1.55±0.01	14.6±0.6	1.73±0.01	16.6±1.0
(8,3)	0.78	0.83±0.00	22.9±1.0	1.06±0.00	16.1±1.0	1.34±0.01	15.5±1.3	1.46±0.00	21.9±1.4
(7,5)	0.83	1.48[§]	156[§]	1.55±0.01	18.0±1.3	1.74[§]	112[§]	1.84±0.02	46.6±13.2
(8,4)	0.84	1.37±0.08	43.2[§]	1.18±0.01	20.0±2.0	1.40±0.02	36.4±6.6	1.44±0.01	36.5±4.0
(10,2)	0.88	1.56±0.01	32.6±5.6	1.74[§]	106[§]	1.94±0.03	27.6±4.1	1.60±0.02	11.2±1.2
(7,6)	0.89	0.85±0.02	9.9±1.5	0.95±0.01	26.8±4.2	1.10±0.01	12.7±1.1	1.23±0.00	28.9±2.7
(11,1)	0.92	1.35±0.05	7.1±1.6	1.34±0.03	7.0±0.9	1.61±0.02	8.9±1.0	1.46±0.02	11.9±1.4
(9,4)	0.92	1.45±0.00	592[§]	1.32[§]	152[§]	1.50±1.49	133[§]	1.24±0.02	14.5±2.5
(10,3)	0.94	0.77±0.01	17.1±2.4	0.96±0.01	15.3±1.5	1.18±0.01	9.8±1.1	1.31±0.01	14.4±1.8
(8,6)	0.97	0.70[§]	282[§]	0.69±0.01	16.1±2.7	0.87±0.01	14.8±1.3	0.98±0.01	44.7±16.2
(9,5)	0.98	0.70±0.01	106[§]	0.76±0.00	16.3±1.1	0.91±0.00	25.9±2.7	1.00±0.01	24.7±4.0
(8,7)	1.03	0.73±0.01	13.8±3.0	0.83±0.02	6.4±0.8	0.98±0.02	6.3±0.9	1.08±0.01	15.2±2.8
Average		1.10	17.2	1.05	15.4	1.31	17.2	1.37	23.9

(C) FMN to SDS replacement on SWNTs.

Assignment (*n*,*m*)	Diameter [nm]	10 °C		20 °C		30 °C		40 °C	
		$K_{FMN\text{-}SDS}$	γ	$K_{FMN\text{-}SDS}$	γ	$K_{FMN\text{-}SDS}$	γ	$K_{FMN\text{-}SDS}$	γ
(6,5)	0.76	0.32±0.00	33.1±3.8	0.43±0.00	64.6±4.9	0.43±0.00	58.7±5.2	0.47±0.00	55.7±7.8
(8,3)	0.78	0.31±0.00	84.3±14.1	0.42±0.00	128.8±16.7	0.41±0.00	112±16.8	0.46±0.00	121±13.7
(7,5)	0.83	0.36±0.01	18.8±3.1	0.47±0.00	62.0±8.3	0.46±0.00	57.7±6.2	0.52±0.01	33.4±5.3
(8,4)	0.84	0.29±0.29	409[§]	0.33±0.02	32.5±9.0	0.37±0.00	120[§]	0.41±0.00	897[§]
(10,2)	0.88	0.46±0.01	17.5±1.9	0.56±0.01	15.4±3.4	0.58±0.01	16.8±2.7	0.73±0.04	17.8±4.5
(7,6)	0.89	0.38±0.01	12.3±1.1	0.48±0.01	21.0±2.5	0.45±0.00	41.8±4.8	0.48±0.00	39.7±5.6
(11,1)	0.92	0.37±0.00	13.0±0.8	0.45±0.00	15.8±2.5	0.45±0.00	12.1±1.1	0.48±0.00	31.2±4.1
(9,4)	0.92	0.46±0.01	8.5±1.1	0.54±0.02	12.5±1.5	0.48±0.00	971.5[§]	0.54±0.54	629[§]
(10,3)	0.94	0.33±0.00	23.7±4.2	0.45±0.00	16.2±3.2	0.44±0.00	29.9±2.8	0.49±0.00	86.9±23.1
(8,6)	0.97	0.22±0.22	1740[§]	0.33±0.00	32.2±4.1	0.32±0.00	59.2±9.7	0.35±0.00	81.5±22.4
(9,5)	0.98	0.31±0.00	22.1±2.5	0.41±0.00	29.0±2.9	0.40±0.00	41.3±5.0	0.44±0.00	48.3±5.9
(8,7)	1.03	0.35±0.01	17.1±4.2	0.43±0.00	41.9±9.2	0.43±0.01	17.9±3.8	0.49±0.01	46.6±22.7
Average		0.35	25.0	0.44	39.3	0.44	44.7	0.49	56.3

[§] values here indicate the uncertainty originating from the sigmoidal transitions occurring within two intervals of titration.

Table S2. Thermodynamic functions (enthalpy, entropy, and Gibbs energy,) derived from van't Hoff equation.

(A) FMN to SDBS replacement on SWNTs.

Assignment (*n*,*m*)	Diameter [nm]	Chiral Angle [Degrees]	Enthalpy (Δ*H*) kJ/mol	Entropy (Δ*S*) J/mol·K	Gibbs Energy (Δ*G*) kJ/mol at 25 °C
(6,5)	0.76	27	7.21±0.85	32.0±2.83	-2.32±1.69
(8,3)	0.78	15.3	6.89±0.64	30.5±2.13	-2.20±1.27
(7,5)	0.83	24.5	4.06±1.57	22.3±5.18	-2.61±3.12
(8,4)	0.84	19.1	6.04±0.71	28.0±2.35	-2.31±1.41
(10,2)	0.88	8.9	3.12±1.01	20.0±3.53	-2.83±2.07
(7,6)	0.89	27.5	6.32±1.19	29.2±3.98	-2.38±2.38
(11,1)	0.92	4.3	4.99±1.09	25.6±3.64	-2.64±2.17
(9,4)	0.92	17.5	5.31±1.12	26.3±3.67	-2.52±2.22
(10,3)	0.94	12.7	7.39±0.55	33.2±1.84	-2.50±1.10
(8,6)	0.97	25.3	6.52±0.42	28.9±1.41	-2.10±0.84
(9,5)	0.98	20.6	6.98±0.33	30.7±1.10	-2.19±0.66
(8,7)	1.03	27.8	7.74±1.14	33.6±3.86	-2.28±2.29
Average			6.05	28.4	-2.41

(B) FMN to SC replacement on SWNTs.

Assignment (*n*,*m*)	Diameter [nm]	Chiral Angle [Degrees]	Enthalpy (Δ*H*) kJ/mol	Entropy (Δ*S*) J/mol·K	Gibbs Energy (Δ*G*) kJ/mol at 25 °C
(6,5)	0.76	27	14.2±2.20	50.2±7.33	-0.75±4.39
(8,3)	0.78	15.3	14.1±1.25	48.4±4.20	-0.32±2.50
(7,5)	0.83	24.5	6.53±0.03	25.9±0.09	-1.20±0.05
(8,4)	0.84	19.1	7.55±1.44	27.2±4.75	-0.56±2.85
(10,2)	0.88	8.9	2.01±2.74	10.9±9.36	-1.25±5.53
(7,6)	0.89	27.5	9.85±0.39	33.2±1.28	-0.05±0.77
(11,1)	0.92	4.3	2.09±3.68	10.1±12.1	-0.93±7.28
(9,4)	0.92	17.5	-2.47±3.07	-6.03±10.3	-0.67±6.14
(10,3)	0.94	12.7	13.2±1.03	44.7±3.49	-0.10±2.08
(8,6)	0.97	25.3	12.5±2.04	39.7±6.69	0.61±4.04
(9,5)	0.98	20.6	9.88±1.18	31.6±3.95	0.45±2.35
(8,7)	1.03	27.8	9.60±0.49	31.3±1.64	0.26±0.98
Average			8.25	28.9	-0.38

(C) FMN to SDS replacement on SWNTs.

Assignment (*n*,*m*)	Diameter [nm]	Chiral Angle [Degrees]	Enthalpy (Δ*H*) kJ/mol	Entropy (Δ*S*) J/mol·K	Gibbs Energy (Δ*G*) kJ/mol at 25 °C
(6,5)	0.76	27	7.99±4.48	19.6±15.1	2.14±8.99
(8,3)	0.78	15.3	9.04±3.44	22.7±11.7	2.27±6.92
(7,5)	0.83	24.5	4.08±3.87	7.23±13.0	1.92±7.75
(8,4)	0.84	19.1	7.21±0.21	15.6±0.68	2.56±0.41
(10,2)	0.88	8.9	8.70±2.06	24.4±7.03	1.41±4.15
(7,6)	0.89	27.5	4.17±2.38	7.24±7.76	2.01±4.70
(11,1)	0.92	4.3	5.42±1.99	11.4±6.70	2.03±3.99
(9,4)	0.92	17.5	-0.30±2.49	-7.08±8.22	1.81±4.94
(10,3)	0.94	12.7	9.81±2.29	25.6±7.75	2.18±4.60
(8,6)	0.97	25.3	3.16±2.54	1.15±8.36	2.82±5.03
(9,5)	0.98	20.6	7.37±3.11	16.9±10.4	2.34±6.21
(8,7)	1.03	27.8	7.01±2.82	16.6±9.54	2.07±5.66
Average			6.14	13.4	2.13

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