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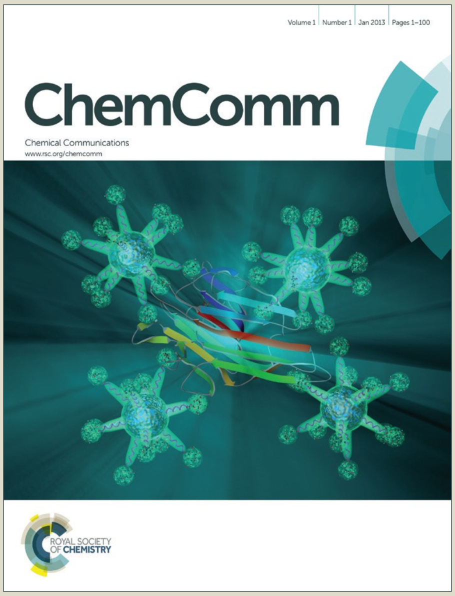

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RESPONSES TO REVIEWERS COMMENTS

We would like to thank the reviewers for their constructive criticisms of our manuscript. We have addressed the reviewers' comments and made necessary changes with the goal of improving both the clarity and quality of the manuscript. The following are our responses to each of the comments and questions raised by the reviewers as well as the different actions taken to address them.

Referee 1: *This manuscript described a detailed study on desorption of specific single walled carbon nanotubes from hydrogels. The experimental results show that the desorption of (6,5) nanotubes occurs at a very specific ratio of SDS/DOC. The authors proposed that this is related to a specific thermodynamic equilibrium state. They further determined the equilibrium constant. The selective separation of single walled carbon nanotubes is important for potential applications of nanotubes. A better understanding of this process is of great scientific values. The results of this work suggest new ideas to understand this process. I would support the publication of this manuscript after the authors address the following issues:*

1. *As the authors mentioned, the extended elution of the (6,5) nanotube is related to length differentiation. The authors should provide more detailed information about the length distribution of (6,5) nanotubes. Especially, have then observed the change in length distribution of (6,5) nanotubes obtained at different elution time?*

> **Response:** The reviewer is correct in stating that we do not provide length measurements of the SWCNTs used in this study. A previous study by Shinohara's group showed that the elution order of arc discharge s-SWCNTs was according to their length, as measured from AFM images (*Appl. Phys. Express* **2013**, 6, 065101). While their first fraction was not a pure (*n*,*m*) type due to differences in the elution characteristics, the size exclusion effects described in their paper could be the same given the similarity in column width and height between our study and their published work.
>
> While we would like to demonstrate the length-dependency of elution, the amount of nanotubes separated was small due to the scale of our column. The figure below (added to supplemental information) shows the elution profile for the 15:1 binary concentration throughout the extended elution. From the additional figure, we observe that the concentration of (*6,5*) nanotubes quickly falls with longer elution times. Although we can observe that there is a continuous elution of (*6,5*) nanotubes, the suspension becomes too dilute to characterize. In principle, we could run these experiments with larger columns to obtain enough material to analyze. However, chromatography often encounters unique issues associated with scale-up that would require a detailed study.
>
> In response to the reviewer's comment, we have clarified our findings and the discussion related to the prior work within the manuscript. We have also added a figure to the Supporting Information.

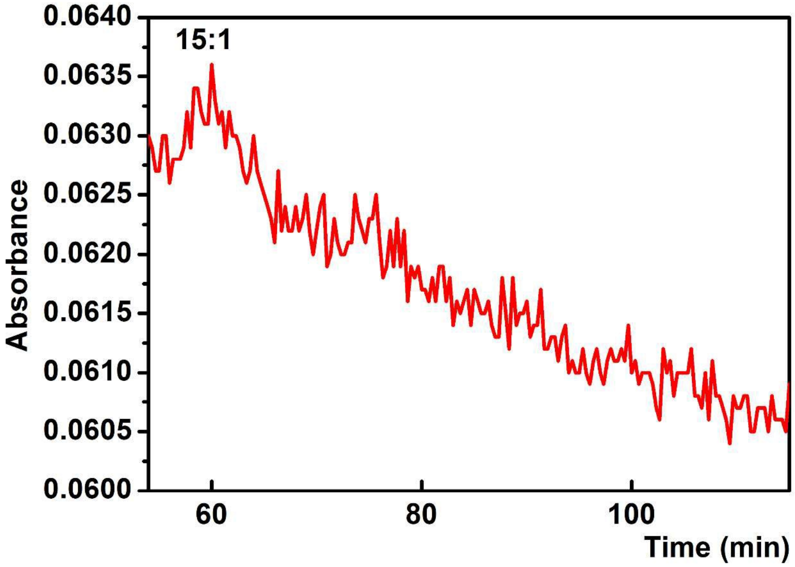

Figure S2a. Elution curve of SWCNTs suspended in 35.0 mM SDS with Sepharose 6 FF as the stationary phase. The elution curve is presented in terms of absorbance of effluent normalized by absorbance of initial suspension (λ = 626 nm). Note that (6,5) SWCNTs are continuously eluted but the concentration falls quickly.

2. *What would be the total yield of (6,5) nanotubes from this process? It seems to me that most of the nanotubes will exist in the multiple adsorbed layers. Only very small portion would be directly adsorbed on the hydrogel surface. Thus, the yield of (6,5) nanotubes could be very low.*

Response: Indeed, the presence of multilayer adsorption hinders the yield since these nanotubes cannot be separated. However, our estimated yield of high purity (*6,5*) is approximately 15%, which is comparable or better than the few yields reported in the literature. We believe we are able to obtain comparable or better yields because we have eliminated the dilution effects associated with multiple columns. More importantly, these multilayers hinder the ability to modulate the interactions between the SWCNTs and the hydrogel with changes to the surfactant structure. Therefore, the need to remove loosely-bound multilayers described in this manuscript is an important finding that eliminates non-selective interactions and enables high-purity separations to be achieved by desorption alone. The high-purity fraction of (*6,5*) SWCNTs obtained in this manuscript serves as a great example of the selective interactions obtained for a specific thermodynamic state. While improved loading of SWCNT monolayers on the hydrogel would improve the yield, these studies are outside the scope of this communication.

In response, we have included a statement about the estimated yield of our collected fraction.

3. *(9,1) nanotubes always come out together with (6,5) nanotubes at a lower concentration. Why other nanotube species at similar diameter are not observed? Does the proposed thermodynamically –stable surfactant structure depend on the diameter of nanotubes?*

Response: We anticipate that each (*n*,*m*) type will have a unique thermodynamic state that determines at what concentration it will start to desorb from the column. The (9,1) species is a minor component of the mixture, making it difficult to determine the specific ratio associated with this species. It is likely that the desorption process for the (9,1) nanotubes occurs at very similar ratios to the (6,5) nanotubes, requiring very small modulations to the surfactant structure to separate these two species. Indeed, Figure 3b does show that some fractions are free of the (9,1) nanotubes Further analysis is underway to determine if these two species can be separated reproducibly by modulating the surfactant structure. Recently, we have started to observe the desorption of other (*n*,*m*) types at other co-surfactant ratios. The preliminary results suggest that the elution order is approximately diameter-dependent with some deviation associated with the mod number. This will be the topic of another manuscript.

Referee 2: *In this manuscript, the authors describe a modified hydrogel-based procedure for selectively separating single-chirality (6,5) single-walled carbon nanotubes (SWNTs) from a mixture. They found that a surfactant mixture of sodium dodecyl sulfate and sodium deoxycholate at a specific concentration ratio allows for the separation of highly pure (6,5) SWNTs with a single chromatography column. The manuscript is well written and easy to follow. However, several questions should be addressed before this manuscript is worthy of publication in ChemComm.*

1. *A recently published paper by Jain et al. in the Journal of Physical Chemistry C (J. Phys. Chem. C, **2015**, 119, 22737-22745) studies the use of mixed surfactant systems for SWNT separation and extends a previously published model to address these new systems. Please comment on how the results presented in this manuscript relate to those reported by Jain et al.*

Response: The paper by Jain et al. focuses on the selective ***adsorption*** of SWCNTs in co-surfactant solutions. These separations require multiple columns (typically greater than 8) while our study is based on the selective ***desorption*** of SWCNTs in a single column. Jain et al. find that the adsorption of SWCNTs to Sephacryl in their systems is kinetically-controlled. On the other hand, we find that the desorption of SWCNTs from Sepharose is thermodynamically-controlled. However, it is important to note that these two papers are describing different processes on different hydrogels. Interestingly, Jain et al. conclude that the SDS+DOC co-surfactant solutions cannot be used to separate the semiconducting SWCNTs. In contrast, we show that these co-surfactant systems are able to achieve high-purity (6,5) SWCNT suspensions. A summary of the differences are shown in the table below:

	This study	**Jain et al.**
Approach	Selective desorption of semiconducting SWCNTs by eluting with co-surfactant solutions	Selective adsorption of semiconducting SWCNTs suspended in co-surfactant solutions
Controlling principle	Thermodynamic states formed during surfactant exchange.	Kinetic effects of SWCNTs after surfactant exchange has occurred.
Column Packing Materials	Sepharose 6FF	Sephacryl

Elution Type	Single column separation	Multi-Column Separation

In response to the reviewer's comment, we have pointed out in the manuscript that there are differences between the adsorption and desorption processes.

2. *The first part of the manuscript (including Figure 1) suggests that a SDS:DOC ratio of 15:1 is optimal for separation of (6,5) SWNTs, however Figure 3c suggests that a ratio of 12.1:1 is optimal. Can the authors comment on this difference?*

Response: We would like to thank the reviewer for pointing out this error. We had errantly listed the slope of the fitted line rather than the true ratio we determined from our fit. We have inserted the correct number into the manuscript and it is indeed close to the value of 15:1.

3. *Also, did the authors experiment with further increasing the concentration of DOC to achieve SDS:DOC ratios less than 10:1? Have the authors tried to separate another chirality of SWNTs from the same column once all of the (6,5) nanotubes have been removed?*

Response: Recently, we have started to observe the desorption of other (*n*,*m*) types at other co-surfactant ratios. The preliminary results suggest that similar thermodynamic states are formed with other (*n*,*m*) types. This communication focuses on the formation of these thermodynamic states. The step-by-step separation of other (*n*,*m*) types will be the topic of another full manuscript.

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COMMUNICATION

Selective Desorption of High-Purity (*6*,*5*) SWCNTS from Hydrogels through Surfactant Modulation

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Selective desorption of (*6*,*5*) single-wall carbon nanotubes from hydrogels only occurs at specific co-surfactant ratios. High-purity fractions are obtained at this ratio even with long elution times and different total co-surfactant concentrations. These results suggest each (*n*,*m*) type forms a thermodynamically-stable surfactant structure in the co-surfactant solution, enabling high-fidelity separations in a single column.

The synthesis of single-walled carbon nanotubes (SWCNTs) yield a complex mixture of species with different properties defined by their (*n*,*m*) chiral indices.[1,2] The coexistence of metallic (m-) and semiconducting (s-) SWCNTs with varied bandgaps hinders their application, especially in high performance electronic devices. Although some success has recently been reported for selective growth of SWCNTs with a specific chiral index,[3] a simple, large-scale separation of SWCNTs is a highly desirable, application-oriented goal. Over the last several years, various methods have achieved the separation of SWCNTs.[4-8] While each of these techniques are capable of separating SWCNTs, selective adsorption of SDS-suspended SWCNTs on hydrogel surfaces is a simple chromatographic approach that requires minimal preparation work and can achieve large-scale, high-throughput separations.[9,10]

The separation of SWCNTs by selective adsorption or most other methods has been shown to be dependent on the surfactant structure.[11-13] Both experimental[14,15] and theoretical modeling studies[16,17] have shown that the interaction of surfactants with SWCNT surfaces is dynamic and driven by the identity of the surfactant, its concentration, and the chirality of the nanotube. Therefore, subtle alterations to the composition and concentration of the eluent, should gradually modulate the surfactant structure of each SWCNT (*n*,*m*) type and, hence, the strength of interaction between the surfactant-coated SWCNTs and the hydrogel surface. Gui and co-workers applied a binary gradient elution in an attempt to achieve this control over the surfactant structure.[18] While some separation was observed, the fractions still contained multiple (*n*,*m*) types at considerable concentrations.

In this communication, we show that the elution of (*6*,*5*) nanotubes occurs at a very specific ratio of sodium dodecyl sulfate (SDS)/sodium deoxycholate (DOC) co-surfactant solution. High-purity fractions are obtained even with changes to the elution time, total co-surfactant concentration, and temperature. The elution behavior strongly suggests that each (*n*,*m*) type forms a thermodynamically-stable surfactant structure that dictates its interaction with the hydrogel. In contrast to prior hydrogel separations by (*n*,*m*) type, these thermodynamics equilibrium states allow the separation to be conducted on a single column with a single elution profile, providing simpler operation and less dilution of the product.

Similar to our previous work,[11] the metallic fraction is the first to exit the column with 35.0 mM (1 wt%) SDS as the eluent (see Figure 1a). As described previously, the s-SWCNTs remain selectively adsorbed onto the surface of the hydrogel.[12] These SWCNTs can be subsequently removed by changing the eluent to sodium cholate or DOC.[11,12,19] However, very small changes to the elution profile (see Figure 1b) were used here to carefully control the surfactant structures surrounding the SWCNTs. The next fraction to exit the column occurs at a 20:1 ratio of SDS:DOC. Interestingly, this fraction contains nearly all (*n*,*m*) types and the absorbance looks very similar to the initial suspension (see Figure S1). This result would seem to suggest that the selective separation of s-SWCNTs is not feasible. However, the PL spectra in Figure 1c shows that the 15:1 fraction consists of a nearly monochiral (*6*,*5*) suspension with a small amount of (*9*,*1*) contamination.[20] The remarkable part of this elution is that no other (*n*,*m*) types desorb even for extended flow at this concentration for 60 min. Figure 1c shows that (*6*,*5*) nanotubes are continuously

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x eluted from the column over a 52.5 min period. However, the concentration of (*6*,*5*) nanotubes decreased quickly and, more importantly, no other (*n*,*m*) types can be observed even at long elution times. The fact that no other species desorb under continued exposure to DOC indicates that there is no significant accumulation of the surfactant on other (*n*,*m*) types. The remaining s-SWCNTs adsorbed onto the hydrogel can then be eluted once the surfactant structure is modulated enough to force desorption from the hydrogel.

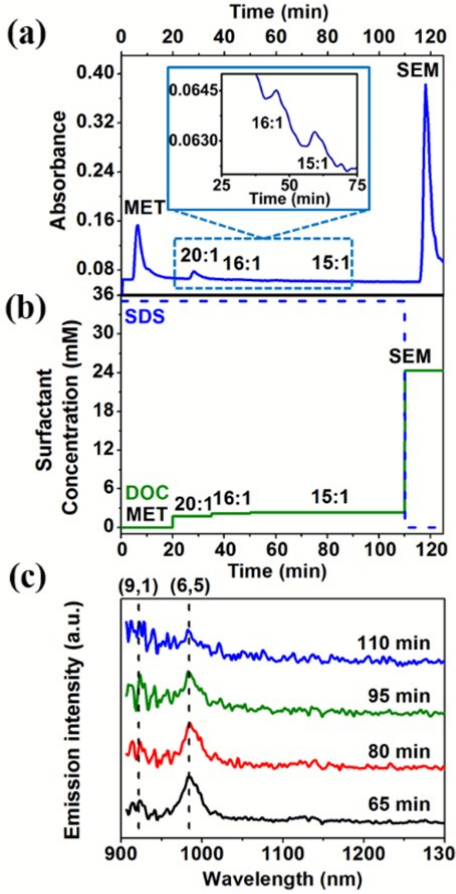

Fig. 1 (a) Elution curve of SWCNTs suspended in 35.0 mM SDS with Sepharose 6 FF as the stationary phase. The SWCNT suspension is injected at time 0. The elution curve is presented in terms of absorbance of effluent normalized by absorbance of initial suspension (λ = 626 nm). (b) Elution profile demonstrating the specific SDS:DOC ratios used in the separation. (c) Corresponding fluorescence spectra (excited at 662 nm) of s-SWCNTs fractions collected during elution with SDS:DOC ratio of 15:1 at 15 min time intervals. Fluorescence (excited at 784 nm) and absorbance spectra also confirmed the monochiral fraction with high purity, as shown in Figure S2.

The transition from elution of all s-SWCNT (*n*,*m*) species at a 20:1 ratio to the elution of a monochiral (*6*,*5*) suspension at a 15:1 ratio indicates a complex process occurring on the surface of the hydrogel. In our previous equilibrium studies, non-Langmuir adsorption was observed for SWCNTs onto the surface of hydrogels.[11,12] These adsorption processes indicate that adsorption sites have different locations/conformations producing various energy barriers to adsorption. Given the one-dimensional structure of nanotubes and the shape of the isotherms, multilayer adsorption seems highly likely. The presence of multilayers would significantly hinder the ability to tune the interactions between the SWCNTs and the hydrogel with changes to the surfactant structure. These difficulties are due to the fact that the strength of interaction is dependent on the distance between the nanotube and hydrogel surface.[11] Therefore, the SWCNTs on the outer layers of the multilayer would have weak, non-selective interactions.

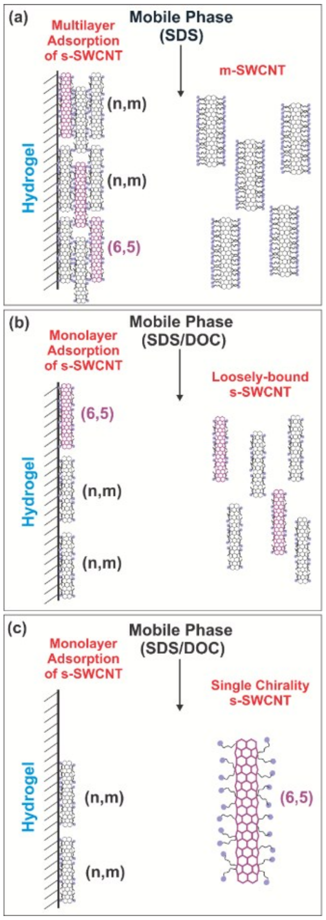

Fig. 2 Schematic for the hydrogel-based separation of SWCNTs using selective adsorption and desorption. (a) Multilayer adsorption of s-SWCNTs while m-SWCNTs are eluted. (b) Removal of loosely-bound SWCNTs from the surface of the hydrogel. (c) Isolation of single-chirality (*6*,*5*) SWCNTs by selective desorption at specific SDS:DOC ratios.

An updated mechanism for the adsorption-desorption process is presented in Figure 2. The first step shown in Figure 2a is the selective adsorption of s-SWCNTs that enable the elution of m-SWCNTs with only SDS. Contrary to our previous schematic,[12] the s-SWCNTs are shown as a multilayer on the surface. A small change to the mobile phase displaces the weakly-bound s-SWCNTs, leaving a monolayer of tightly-bound nanotubes on the hydrogel, as shown in Figure 2b. This step explains why the second peak in the elution curve of Figure 1a (20:1 ratio) yields a broad distribution of (*n*,*m*) species. Finally, Figure 2c shows that single-chirality separation with different surfactant structures is now possible. Figure 1c indicates that a high-purity fraction of (*6*,*5*) SWCNTs is the first to be released from the column after the removal of the loosely-bound SWCNTs. The extended elution of the (*6*,*5*) nanotubes could be associated with length differentiation by size exclusion, which was observed by Shinohara and co-workers during desorption from the column.[21] Interestingly, other (*n*,*m*) types remain tightly-adsorbed to the hydrogel during this long elution until the DOC concentration is increased.

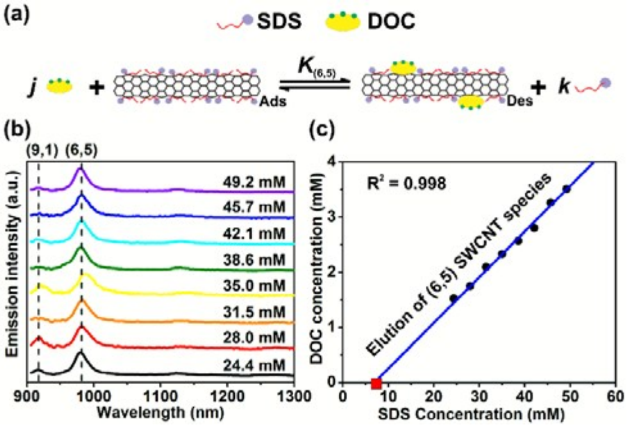

Fig. 3 (a) The equilibrium state of (*6*,*5*) SWCNTs and surfactant in the SDS/DOC co-surfactant elution systems (Ads, Adsorption; Des, Desorption). (b) Fluorescence spectra (excited at 662 nm) of s-SWCNTs fractions collected during elution with SDS/DOC co-surfactant solution at different background SDS concentrations between 24.4 and 49.2 mM. All the effluents were collected at 10 °C with an elution interval of 15 min. Fluorescence (excited at 784 nm) and absorbance spectra also confirmed the monochiral fraction with high purity, as shown in Figure S3. (c) Relationship between DOC and SDS concentrations required to elute high-purity (*6*,*5*) fractions. The fitted line has a near perfect correlation indicating the formation of a thermodynamic equilibrium state. The red square represents the CMC value of pure SDS.

The stability of the desorption of (*6*,*5*) nanotubes despite extended exposure to DOC strongly suggests that a specific thermodynamic equilibrium state is formed for the surfactant structure surrounding each nanotube. Figure 3a shows what this equilibrium state may look like in these systems. The stoichiometric coefficients for the free DOC (*j*) and SDS (*k*) are unknown since it is possible that the DOC displaces some of the SDS or simply adds to the SDS already on the surface. The equilibrium constant, $K_{(6,5)}$, would then be described by $K_{(6,5)} = \left(c_{SWCNT}^{Des}/c_{SWCNT}^{Ads}\right)\cdot\left(c_{SDS}^{k}/c_{DOC}^{j}\right)$, where c is the concentration of each species. Since the nanotube concentration remains constant in this reaction, the equilibrium constant is simplified to $K_{(6,5)} = c_{SDS}^{k}/c_{DOC}^{j}$. In order to determine the stoichiometric coefficients and the equilibrium constant, the concentration of DOC required to desorb the (*6*,*5*) nanotubes under different SDS concentrations was examined. Figure 3b shows the PL spectra for the fractions containing the (*6*,*5*) SWCNTs at these different SDS concentrations. A single chirality (*6*,*5*) fraction is still the first fraction to be eluted out at all SDS concentrations once the multilayer SWCNTs are removed. The spectra show that high-purity (*6*,*5*) fractions can be obtained at a variety of SDS concentrations. The corresponding fluorescence spectra (excited at 784 nm) and absorbance spectra also confirm the high purity of the (*6*,*5*) fraction, as shown in Figure S3. The fraction has a purity of 90 % and an estimated yield of (*6*,*5*) SWCNTs of 1.6 %. There may be a slight tendency for better purity (fewer (*9*,*1*) nanotubes) at higher concentrations but this could be related to sample collection. Figure 3c shows the corresponding DOC concentration when the (*6*,*5*) nanotubes are eluted at each SDS concentration. As the figure illustrates, there is a nearly perfect linear correlation (R^2 = 0.998) between the surfactant concentrations needed to elute the (*6*,*5*) nanotubes. Although a reasonable fit can also be obtained with a power law, the power is very close to a value of 1. Therefore, both fits suggest that the stoichiometric coefficients are equivalent (*j* ≈ *k*), yielding $K_{(6,5)}$ = 15.1. More importantly, the data demonstrate that there is a very specific ratio of surfactant concentration required to elute the (*6*,*5*) nanotubes regardless of the concentration of SDS used. An interesting feature of this relationship is that the fitted line seems to go through the CMC point of pure SDS. Taken together, there is strong evidence that the desorption behavior is related to thermodynamic equilibrium states. Note that the desorption process can be different from the adsorption process described by others.[10]

Once the equilibrium constant is known, other thermodynamic parameters, such as the standard molar Gibbs free energy for desorption, can be determined $\left(\Delta G^{\circ,Des} = -RT\ln K_{(6,5)}\right)$. The Gibbs free energy is related to the enthalpy and entropy changes for the desorption reaction, $\Delta G^{\circ,Des} = \Delta H^{\circ,Des} - T\Delta S^{\circ,Des}$. Therefore, a van't Hoff plot $(\ln K_{(6,5)}\ vs.\ 1/T)$ enables determination of the enthalpy and entropy changes from the slope and intercept, respectively. Figure 4 shows fluorescence spectra (excited at 662 nm) of the fractions containing the (*6*,*5*) nanotubes while maintaining the column at a temperature of 10, 15, or 20 °C. The corresponding fluorescence spectra (excited at 784 nm) and absorbance spectra also confirmed the separated fraction of high purity (*6*,*5*) SWCNTs, as shown in Figure S4. The SDS:DOC ratio required to elute the (*6*,*5*) nanotubes remained constant at all temperatures, indicating that the desorption process is insensitive to temperature at an SDS concentration of 35.0 mM. Assuming that the slope of Figure 3c is also insensitive to temperature changes at other concentrations, $K_{(6,5)}$ and, thus, $\Delta G_{(6,5)}^{\circ,Des}$ can be considered to be approximately constant. Therefore, the slope of the van't Hoff plot would be approximately zero or $\Delta H^{\circ,Des}{\sim}0$, indicating that the desorption process for the (*6*,*5*) nanotubes is predominantly driven by entropy changes, or $\Delta G^{\circ,Des} \approx -T\Delta S^{\circ,Des}$.

These entropy changes will likely be related to the structural changes associated with water molecules forming around different surfactants on the nanotube.[12,22,23]. Note that this analysis does not mean that enthalpic processes are irrelevant to the adsorption differences described previously for m- and s-SWCNT adsorption processes.[12,24] It means that the interaction energy between the (*6*,*5*) nanotubes and hydrogel at different temperatures are not significant and that the entropy changes associated with the addition of DOC drive the desorption process. The adsorption process only involves SDS and must be described by a different reaction in which enthalpy and entropy likely have a key role.

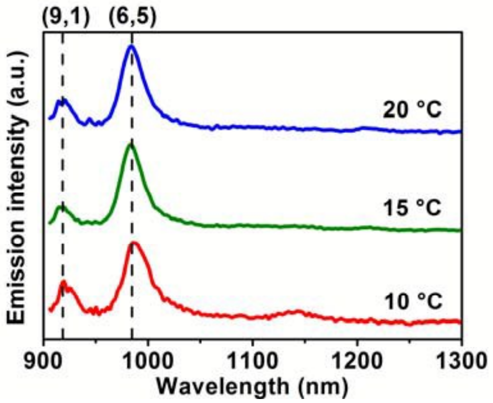

Fig. 4 Fluorescence spectra (excited at 662 nm) of s-SWCNTs fractions collected during elution with an SDS:DOC ratio of 15:1 at temperatures of 10, 15, and 20 °C. Fluorescence (excited at 784 nm) and absorbance spectra also confirmed the monochiral fraction with high purity, as shown in Figure S4.

In conclusion, we demonstrate the formation of thermodynamically-stable co-surfactant states around SWCNTs that enable the desorption of (*6*,*5*) nanotubes for high-fidelity separations in a single-column packed with hydrogel. A key feature of the separation is the removal of SWCNTs that have formed a multilayer on the hydrogel surface. Once these loosely-bound SWCNTs are removed from the surface, the selective elution of (*6*,*5*) nanotubes occurs at very specific surfactant ratios even with extended elution times, different total co-surfactant background concentrations, and moderate temperature changes. Since no other (*n*,*m*) types elute at this specific surfactant ratio, desorption is not based on the accumulation of DOC on the surface of the nanotube but is related to specific thermodynamic states formed at each surfactant ratio. The formation of these thermodynamically-stable surfactant states surrounding SWCNTs provides significant benefits over other published separations based on selective adsorption alone. The formation of specific thermodynamic states allows more precise and effective control of the elution strength needed to remove each (*n*,*m*) type when compared to elution with increased SDS concentrations,[9] different pH,[25] or under different temperatures.[26] The separation can also be conducted in a single column, which simplifies the process and reduces the dilution that occurs during elution of a specific (*n*,*m*) type. The selective adsorption-desorption process described here provides a promising foundation for the development of a large-scale, single-column separation that can collect each (*n*,*m*) type.

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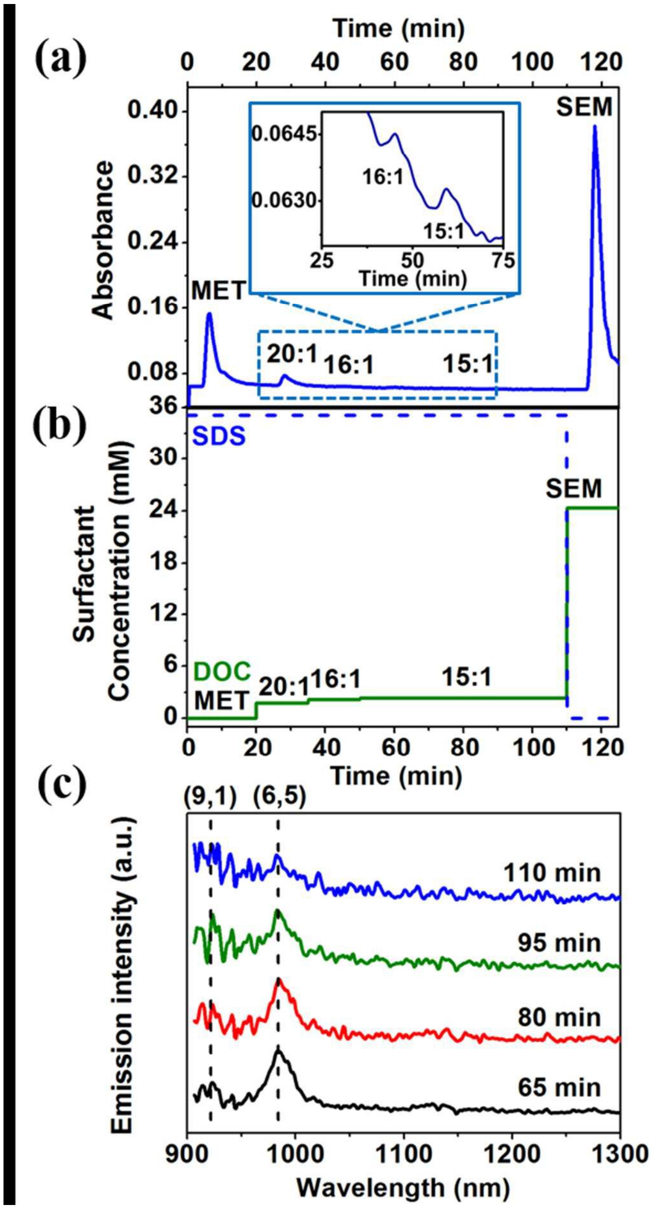
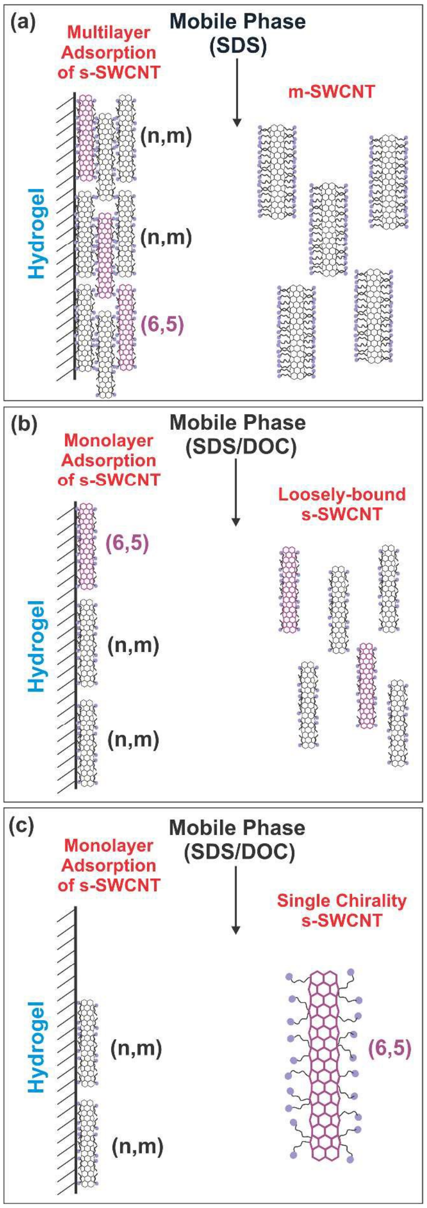
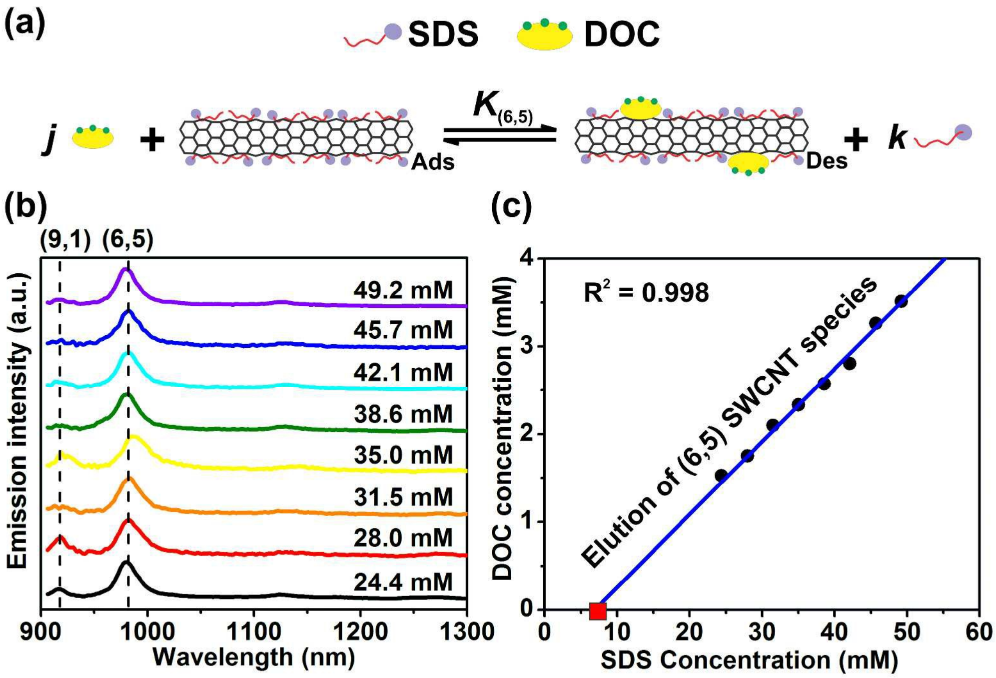
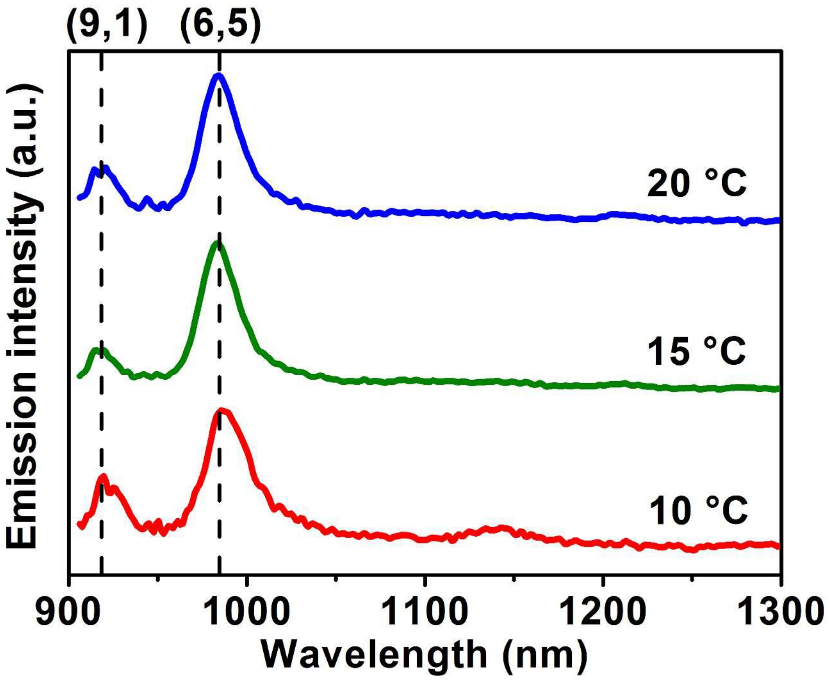
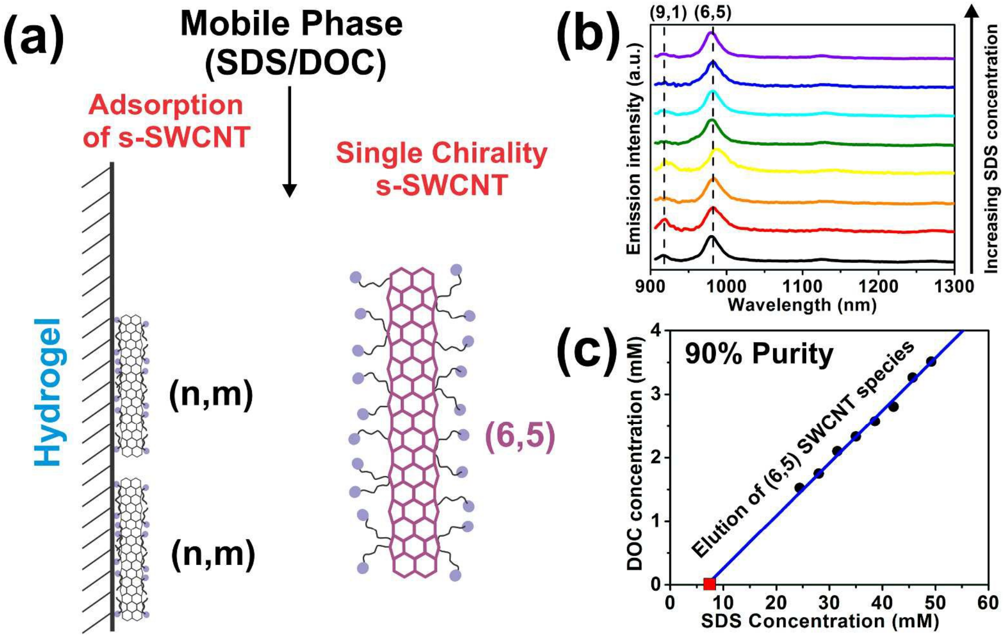

(a)
Time (min)
0 20 40 60 80 100 120
Absorbance
0.40 0.32 0.24 0.16 0.08
SEM
MET
20:1
16:1
15:1
0.0645
0.0630
16:1
15:1
25 50 75
Time (min)
(b)
36 30 24 18 12 6 0
Surfactant Concentration (mM)
SDS
SEM
DOC
MET
20:1
16:1
15:1
0 20 40 60 80 100 120
Time (min)
(c)
(9,1)
(6,5)
Emission intensity (a.u.)
110 min
95 min
80 min
65 min
900 1000 1100 1200 1300
Wavelength (nm)


(a)
Multilayer Adsorption of s-SWCNT
Mobile Phase (SDS)
m-SWCNT
(n,m)
(n,m)
(6,5)
Hydrogel
(b)
Monolayer Adsorption of s-SWCNT
Mobile Phase (SDS/DOC)
Loosely-bound s-SWCNT
(6,5)
(n,m)
(n,m)
Hydrogel
(c)
Monolayer Adsorption of s-SWCNT
Mobile Phase (SDS/DOC)
Single Chirality s-SWCNT
(n,m)
(n,m)
(6,5)
Hydrogel


(a)
SDS
DOC
j
+
Ads
K(6,5)
Des
+ k
(b)
(9,1)
(6,5)
49.2 mM
45.7 mM
42.1 mM
38.6 mM
35.0 mM
31.5 mM
28.0 mM
24.4 mM
Emission intensity (a.u.)
900
1000
1100
1200
1300
Wavelength (nm)
(c)
R² = 0.998
Elution of (6,5) SWCNT species
DOC concentration (mM)
0
1
2
3
4
0
10
20
30
40
50
60
SDS Concentration (mM)


(9,1)
(6,5)
Emission intensity (a.u.)
20 °C
15 °C
10 °C
900
1000
1100
1200
1300
Wavelength (nm)


(a)
Mobile Phase (SDS/DOC)
Adsorption of s-SWCNT
Single Chirality s-SWCNT
Hydrogel
(n,m)
(n,m)
(6,5)
(b)
(9,1) (6,5)
Emission intensity (a.u.)
Increasing SDS concentration
900 1000 1100 1200 1300
Wavelength (nm)
(c)
90% Purity
Elution of (6,5) SWCNT species
DOC concentration (mM)
0 1 2 3 4
0 10 20 30 40 50 60
SDS Concentration (mM)

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Supporting Information for

Selective Desorption of High-Purity (*6,5*) SWCNTS from Hydrogels through Surfactant Modulation

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Materials. Nanopure water (18 mΩ) was used in all experiments. Both SDS (≥ 99%) and DOC (≥ 97%) were purchased from Sigma-Aldrich and used as received. HiPco SWCNTs were obtained from Rice University (HPR 164.1) and used as received. The hydrogel (6FF) was manufactured by GE Healthcare and purchased directly from GE.

Aqueous Suspension Preparation. Aqueous suspensions of SWCNTs were prepared by mixing 30−40 mg of raw SWCNT powder (HPR 164.1) with 150 mL of a 35.0 mM SDS solution in Nanopure water. This solution was mixed at 8000 rpm (IKA T-25 Ultra-Turrax) for 40 min. After homogenization, the solution was allowed to rest for 15 min before cup horn ultrasonication (120 W, Misonix S3000) to aid dispersion. The ultrasonication step was repeated a total of three times to ensure a well-dispersed suspension. The solution was then ultracentrifuged for 4 h at 20 000 rpm (53 000g) to remove metallic catalysts, amorphous carbon, and SWCNT bundles from solution (Beckman Coulter Optima L-80K, SW-28 rotor).

Column Experiments. The single column experiments were completely automated (Chromeleon software), allowing for sample injection, elution gradients, and real-time fraction characterization using an HPLC pump and fluorometer. Sample injection and binary gradient elution were controlled by an HPLC pump (Ultimate 3000, Dionex) with a flow rate of 1 mL/min. The low-pressure chromatography column (Bio-Rad) was made of glass and had an inner diameter of 1.5 cm. The column was packed with 5 mL of agarose beads (Sepharose 6FF) that typically resulted in a column height of 3 cm. An Econo flow adapter (Bio-Rad) connected the column to the HPLC pump. The column and eluents were submerged in a water bath and chilled to 10, 15, or 20 °C. A typical experimental sequence consisted of first stabilizing the column with four column-volumes (CV) of 35.0 mM SDS solution. One-fifth of a CV of the initial suspension was then injected into the column. The metallic SWCNT fraction was collected first by elution with SDS. After removing the metallic fraction, different ratios of SDS/DOC co-surfactant solution were used to modulate the surface properties of the semiconducting SWCNTs adsorbed onto the hydrogel. Collected fractions were characterized by absorption (1.0 cm path) and fluorescence spectroscopy (1.0 cm path) on an Applied NanoFluorescence Nanospectralyzer (Houston, TX) with excitation from 662 and 784 nm diode lasers. Effluent from the column was continuously characterized in situ by use of a flow cell from Starna Cells. Typically, absorption spectra were taken every 20 s while the effluent flowed through the cell. Elution profiles of SWCNTs released from the column were estimated by use of absorbance values at 626 nm to account for the presence of both metallic and semiconducting SWCNT species. A Bio-Rad fraction collector (Model 2110) captured samples every 1.5 CV during elution. The purity of each (*n*,*m*) fraction was computed as the ratio of the area of the dominant peak to the sum of the areas of all peaks.

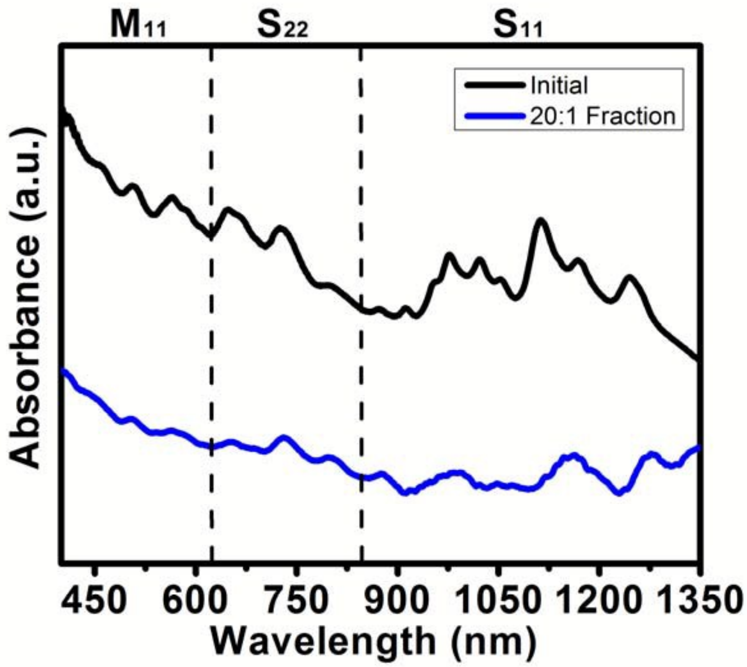

Figure S1. Normalized absorbance spectra (λ = 626 nm) for the initial suspension and effluent collected with SDS:DOC ratio of 20:1. Note: The NIR region of the 20:1 fraction curve has been smoothed to leave out the noise that is caused by dilution. Spectra of the initial and 20:1 fraction have been slightly offset for visual clarity.

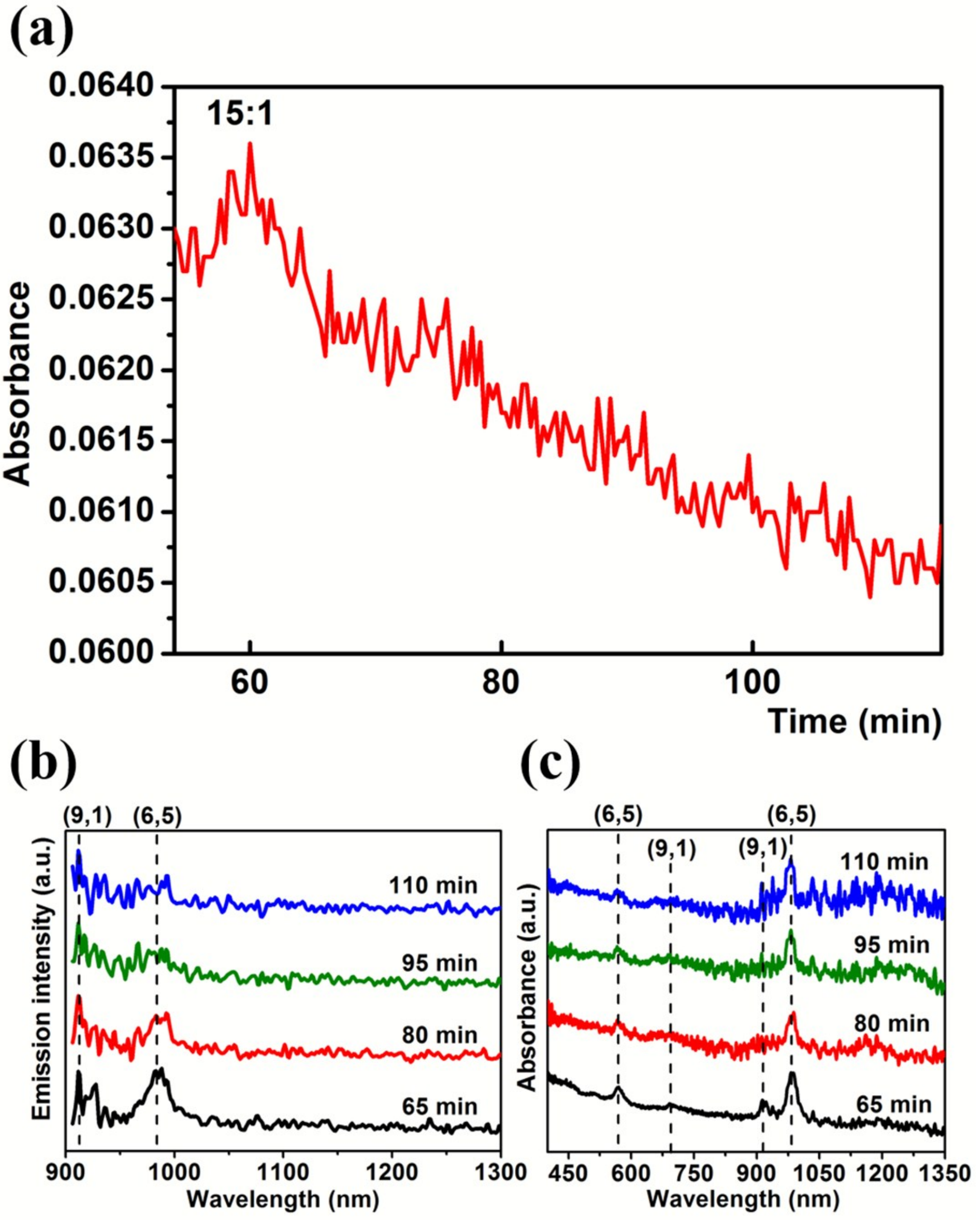

Figure S2. (a) Elution curve of SWCNTs suspended in 35.0 mM SDS with Sepharose 6 FF as the stationary phase. The elution curve is presented in terms of absorbance of effluent normalized by absorbance of initial suspension (λ = 626 nm). Note that (6,5) SWCNTs are continuously eluted but the concentration falls quickly. (b) Fluorescence spectra (excited at 784 nm) of s-SWCNTs fractions collected during elution with SDS:DOC ratio of 15:1 at 15 min time intervals. (c) Corresponding absorbance spectra of the selectively separated s-SWCNTs fractions.

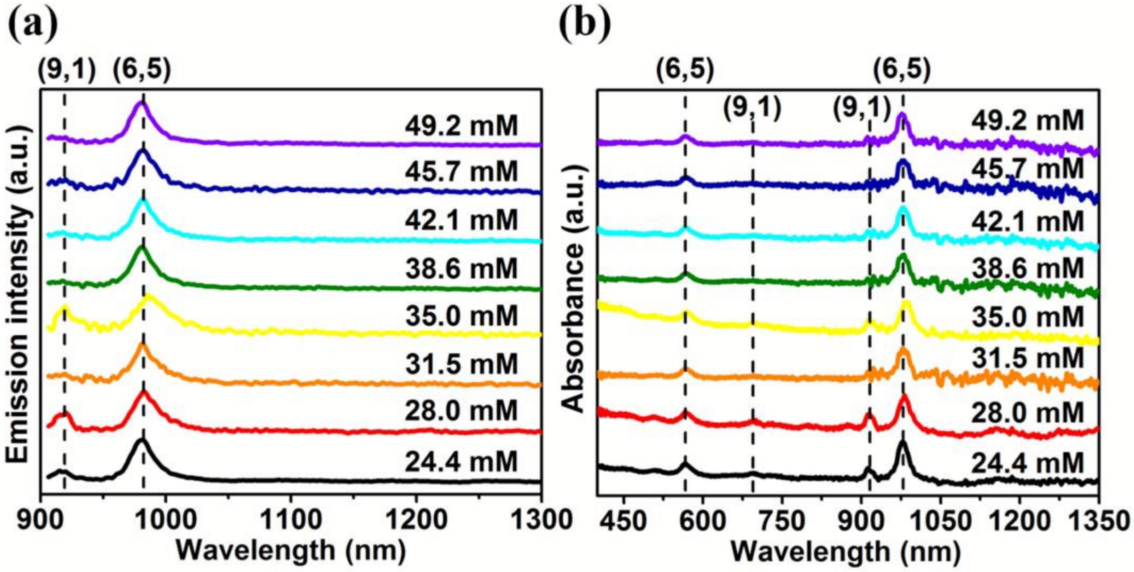

Figure S3. (a) Fluorescence spectra (excited at 662 nm) of s-SWCNTs fractions collected during elution with SDS:DOC co-surfactant solution at different background SDS concentrations between 24.4 and 49.2 mM. All the effluents were collected at 10 °C with an elution interval of 15 min. (b) Corresponding absorbance spectra of the selectively separated s-SWCNTs fractions.

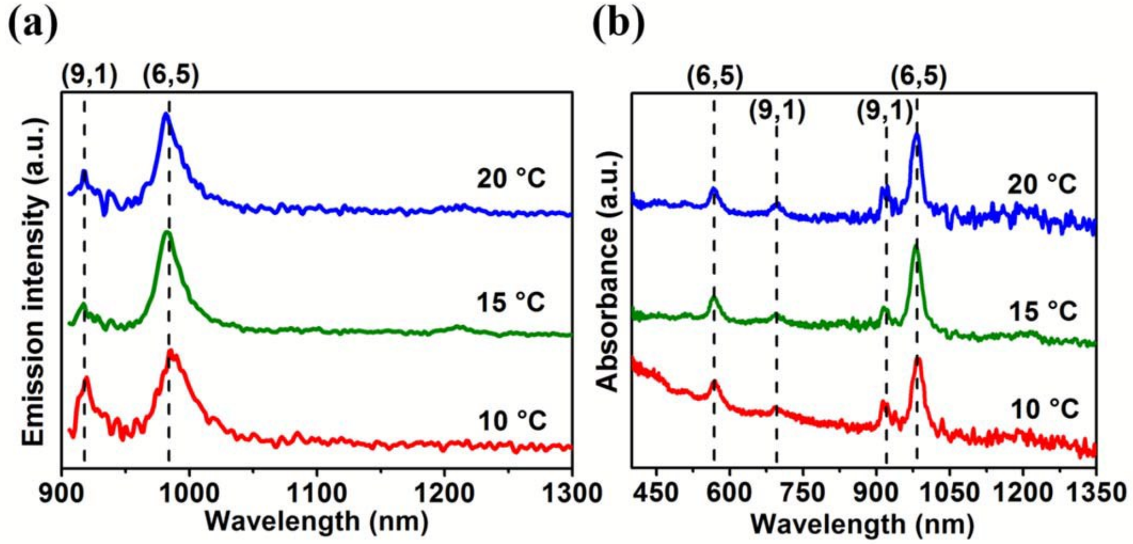

Figure S4. (a) Fluorescence spectra (excited at 784 nm) of s-SWCNTs fractions collected during elution with an SDS:DOC ratio of 15:1 at temperatures of 10, 15, and 20 °C. (b) Corresponding absorbance spectra of the selectively separated s-SWCNTs fractions.


(9,4)
(7,6)
(10,2)
(7,5)
(6,5)
(8,3)
(9,1)
(6,5)
(6,5)
(6,5)
DOC
SDS
H2O


(9,4)
(7,6)
(10,2)
(7,5)
(6,5)
(8,3)
(9,1)
(6,5)
(6,5)
(6,5)
DOC
SDS
H2O