Supporting Information for:

Measuring the Accessible Surface Area within the Nanoparticle Corona using Molecular Probe Adsorption

Authors

Minkyung Park[1], Daniel P. Salem[1], Dorsa Parviz[1], Xun Gong[1], Kevin S. Silmore[1], Tedrick Thomas Salim Lew[1], Duc Thinh Khong[2,3], Mervin Chun-Yi Ang[2], Seon-Yeong Kwak[4], Mary B. Chan-Park[2,3], Michael S. Strano[1]

[1]Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts, United States

[2]Disruptive & Sustainable Technologies for Agricultural Precision IRG, Singapore-MIT Alliance for Research and Technology, 1 Create Way, Singapore 138602, Singapore

[3]School of Chemical and Biomedical Engineering, Nanyang Technological University, 62, Nanyang Drive, Singapore 637459, Singapore

[4]Department of Biosystems and Biomaterials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea

Corresponding Author

E-mail : strano@mit.edu

Phone : +1 (617) 324-4323

Fax : +1 (617) 258-8224

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Method

Materials

Gold nanospheres with different sizes are purchased from nanoComposix. PS beads and CoMoCat SWNT were purchased from Sigma-Aldrich. Expanded graphite (Grade 3806) was provided by Asbury Carbons. Sodium dodecyl sulfate (SDS), Sodium Cholate (SC), Sodium Dodecyl Benzenesulfonate (SDBS), Polystyrenesulfonate (PS), Dextran, Chitosan, polyvinylpyrrolidone (PVP) and riboflavin were purchased from Sigma-Aldrich. ssDNA oligonucleotides including $(GT)_{15}$, $(AT)_{15}$ and $(GTTT)_7$ were purchased from Integrated DNA Technologies.

Preparation of AuNP dispersions

AuNP dispersion was diluted from stock solutions, yielding particle concentration (particle/L) of 9.88×10^{14} for 10nm diameter sizes.

Preparation of PS bead dispersions

PS beads stock dispersions were vortexed thoroughly and diluted to specific concentration using Tween 20 solution (0.1 %).

Preparation of SWNT dispersions

Dispersion of surfactant-SWNT corona phases

Surfactants including SDS, SC and SDBS were dissolved as 2 wt% in 10mL of Nanopure water. SDS/SC mixture was prepared as a final concentration of 1 wt% SDS and 1 wt% SC in 10 mL of Nanopure water. CoMoCat SWNT was added to surfactant solution as a concentration of 1 mg/ml and the mixture was bath sonicated for 10 minutes. It was tip sonicated (Qsonica Q125) using 0.25 in. probe at 8 W for 1 hour in an ice bath. Dispersed solutions were ultra-centrifuged at 153145 g

(Beckman Coulter, SW 55 Ti rotor) for 8 hours at 20 °C to remove remaining aggregates and impurities. Supernatant was carefully separated from the aggregates collected in bottom of tube after the ultracentrifugation.

Dispersion of ssDNA-SWNT corona phases

2 mg of ssDNA oligonucleotide was mixed with 1 mg of CoMoCat SWNT in 1 mL of 100 mM NaCl solution. The mixture was bath sonicated for 10 minutes and tip sonicated using 0.125 in. probe at 4 W for 10 minutes in an ice bath. Then, the solutions were centrifuged twice at 16100 g for 90 minutes. The top 80 % of supernatant was separated from the aggregates after each round of centrifugation.

Dispersion of high MW polymer-SWNT corona phases

Chitosan (Medium MW, deacetylated) was dissolved in 1 vol% acetic acid as a concentration of 2.5 mg/ml and 1mg of CoMoCat SWNT was added to 1mL of chitosan solution. Tip sonication and centrifugation process were done in the same way of preparing ssDNA-SWNT corona phases. PS 70k 30 wt%) and PS 200k (30 wt%) were diluted with Nanopure water into 1 wt%. They were bath sonicated for 10 minutes, followed by tip sonication using 0.25 in. probe at 8 W for 1 hour in an ice bath and incubated for 12 hours at 50 °C. Crude SWNT dispersions were ultra-centrifuged in a SW55 Ti swinging-bucket rotor (Beckman Coulter) at 153145 g for 4 hours at 20 °C. Supernatant was collected after the ultracentrifugation. Dextran wrapping was prepared by utilizing exchange wrapping method. 1 wt% SDS was dissolved in 10mL Nanopure water and CoMoCat SWNT was added as a concentration of 1 mg/ml. The mixture was bath sonicated for 10 minutes, and tip-sonicated in the same way as surfactant-SWNT corona phases. After ultracentrifugation at 153145 g for 8 hours and collection of supernatant, SDS-dispersed SWNT solution was prepared. Then, 10 wt% of dextran was added to the solution and incubated for 12

hours at 50 °C. The solution was added in 3500 MWCO dialysis cassette (Slide-A-Lyzer, Thermo Scientific) and dialyzed in Nanopure water for 3 days to remove SDS molecules.

Preparation of graphene dispersions

The stabilizers, PVP (MW 10,000) and SC, were dissolved in 100 mL of DI water at 1 wt% and 2 wt%, respectively. Expanded graphite was added to the stabilizer solution at 20 mg/mL concentration. The mixture was poured in a 150 ml glass beaker and tip sonicated (Qsonica, Q-700) for one hour using the 0.5 in. probe at 50 % amplitude. This sample was immediately centrifuged at 3000 g (Beckman Coulter, SW 32 Ti rotor) for 4 hours to remove the unexfoliated graphite. The top 80 % of the supernatant was collected as the final dispersion. The UV-vis spectroscopy was used to determine the concentration of graphene in the dispersion. The dispersions were diluted using the 1 wt% PVP and 2 wt% SC solutions to 10mg/L concentration for later experiments.

Collection of UV absorption spectra

UV absorption spectra of AuNPs, SWNT, and graphene dispersions were collected (Shimadzu UV-3101PC) using 1 cm path length quartz cuvette (Starna). All the absorption spectra were background-subtracted using their reference solutions. The concentrations of stock solutions were calculated based on the absorbance at 450 nm for AuNPS, at 632 nm for SWNT, and at 660 nm for graphene. Extinction coefficients of 0.036, 0.0129, 0.0136 ($L\ mg^{-1}cm^{-1}$) were used to determine the concentration of nanomaterial in SWNT, PVP-Graphene, and SC-graphene dispersions, respectively.

Probe fluorescence measurement

Three solutions which include reference solution, free polymer solution, and nanoparticle solution, were prepared. The reference solutions for each corona phase were chosen based on sample preparation. For example, the reference solution for ssDNA-SWNT corona phases were 100 mM NaCl solution and the one for chitosan-SWNT corona phases were acetic acid. Free polymer solutions were prepared by dissolving the same concentration of polymers made for SWNT dispersion. The concentration of AuNP solution was measured based on the UV absorbance at 520nm. SWNT and graphene corona phase solutions were prepared by diluting stock solutions to 10mg/L with free polymer solutions. Riboflavin was dissolved in Nanopure water and its stock solution was prepared by dilution in a concentration range from 0 to 50 μM. 10 μL of riboflavin stock solution was added to 90 μL of nanoparticle solutions, leading to final concentration range from 0 to 5 μM, and mixed with solutions by pipetting. Riboflavin was excited at 460 nm and its emission spectra was collected from 480 nm to 600 nm with 2 nm step size at top reading position (Varioskan flash spectral scanning multimode microplate reader, Thermo Scientific). The wavelength at maximum fluorescence peak was 530-532 nm.

Measurement of nIR fluorescence from SWNT dispersions

SWNT dispersion diluted as 10 mg/L were prepared. 90 μL of the SWNT solutions were added in triplicate to a 96-well plate and 10 μL of riboflavin stock solutions were added to SWNT solutions and mixed well with pipettes. Mixed solutions were excited by a 785 nm laser (450 mW, B&W Tek Inc.) through a 20x objective. nIR fluorescent measurements were taken by an inverted Zeiss AxioVision microscope coupled with a Princeton Instruments InGaAs OMA V array detector through a PI-Action SP2500 spectrometer. Exposure time was varied depending on the SWNT

corona phases, from 0.5 seconds to 8 seconds. All the fluorescence measurements were background-subtracted using their reference solutions.

Calculation of estimated slope value on Equation (14)

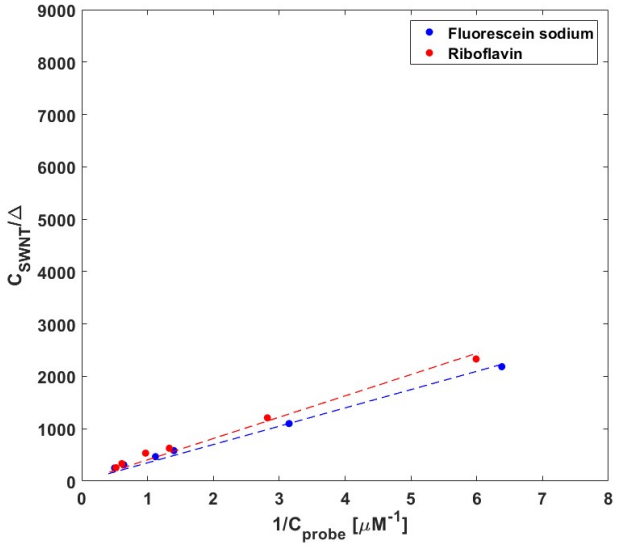
$$\text{Slope} = -\frac{A r_{probe}}{6RT(LhS_{probe}\rho_C)^{1/3}}$$

$$= -\frac{10^{-19} J \times (6.02\times10^{23})\frac{\text{number of molecule}}{mol} \times 0.792nm}{6\times8.314\frac{J}{mol\cdot K}\times293K\times(300nm\times0.5nm\times0.627nm^2\times98.7\frac{\text{number of C atom}}{nm})^{\frac{1}{3}}}$$

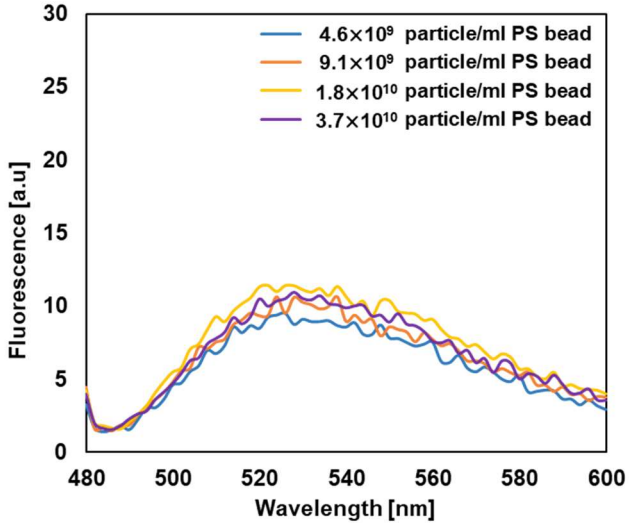
$$= -0.153$$

Hamaker constant (A) was assumed as 10^{-19} J. The radius (r_{probe}) and area (S_{probe}) of the probe were derived from its volume calculated by molecular weight and density. The length of SWNT (L) and height of corona (h) were assumed as 300 nm and 0.5 nm, respectively. Number density of C atom (ρ_C) was calculated based on the graphene surface of CoMoCat SWNT.

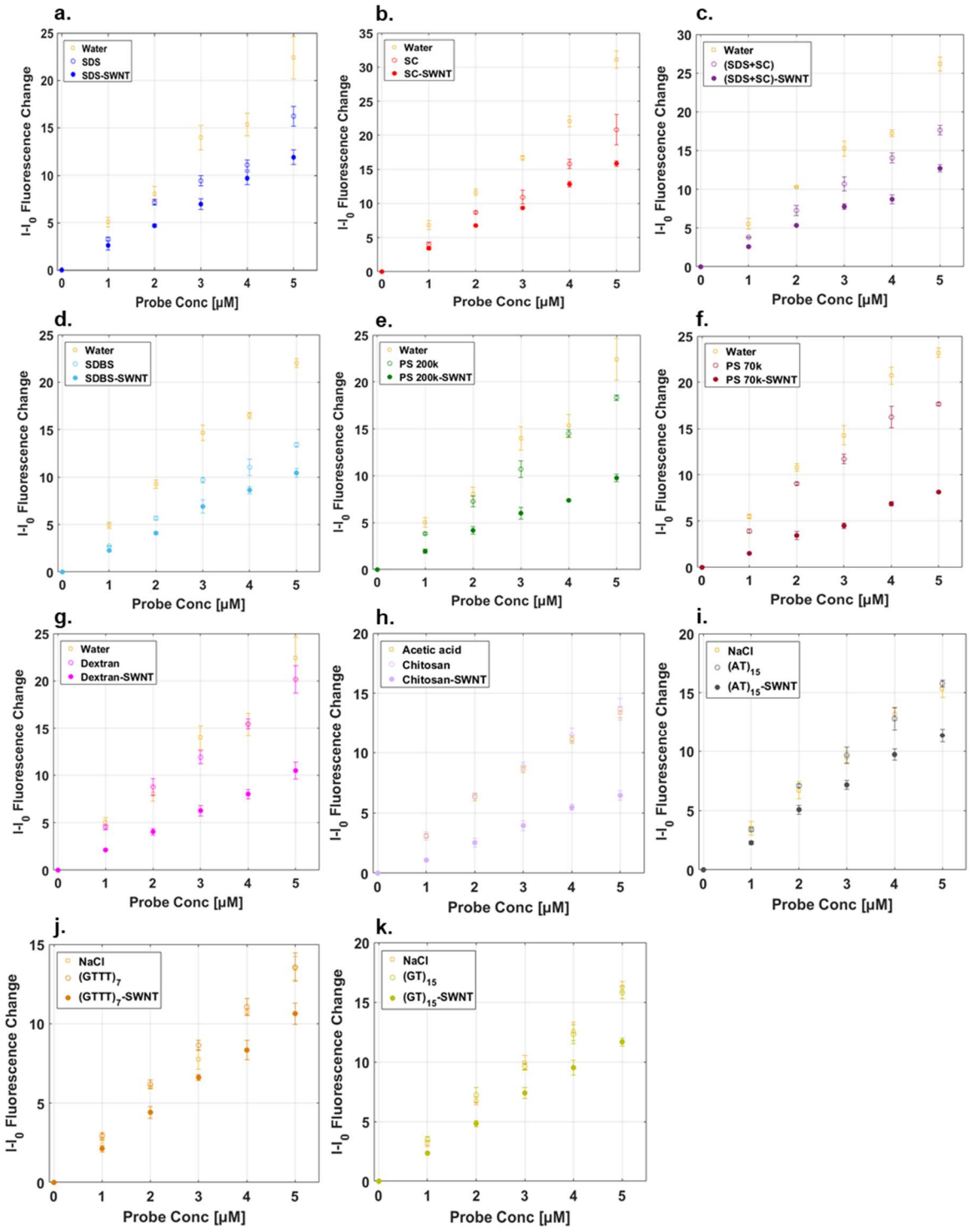
Supplementary Figures



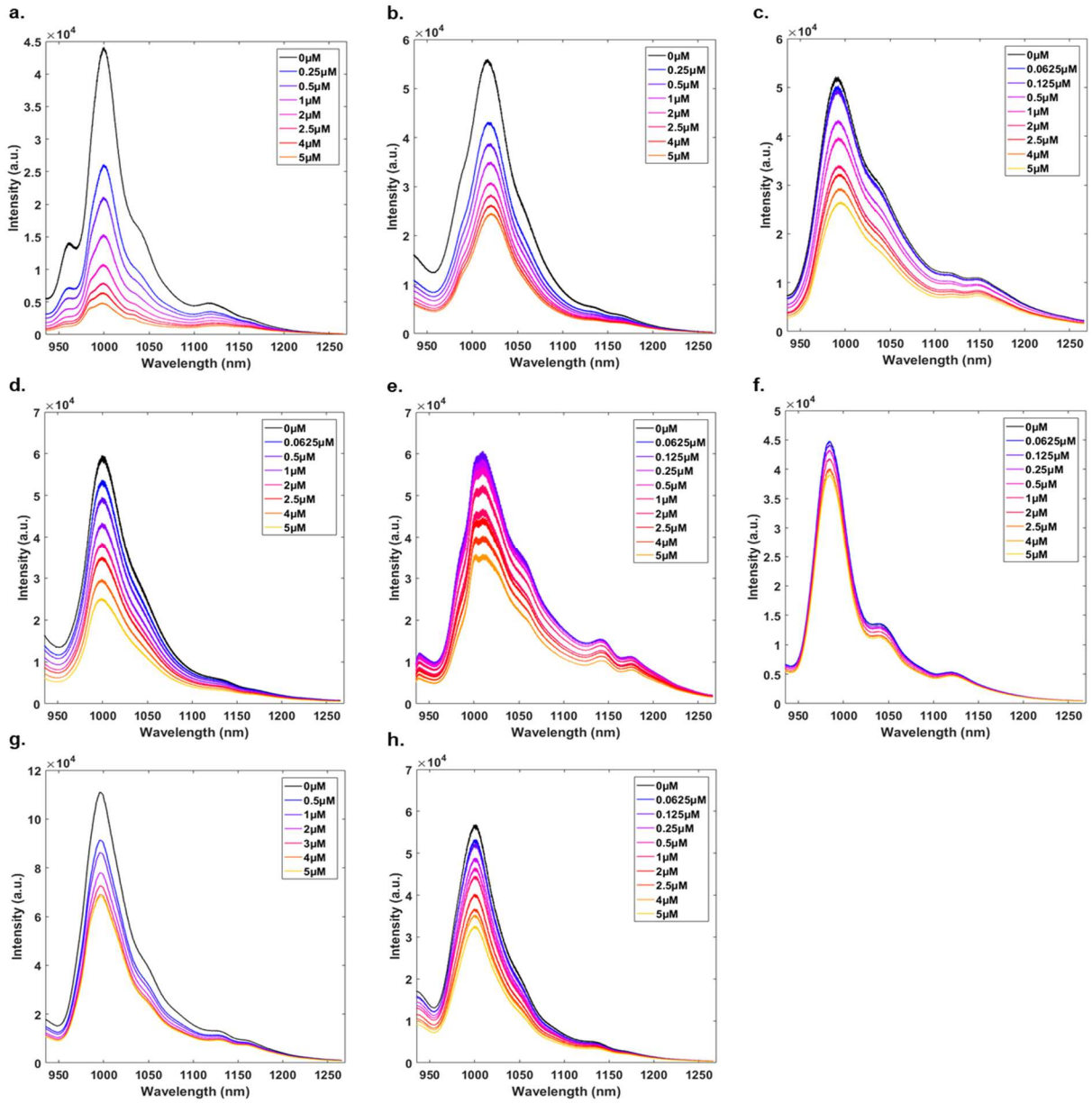
Supplementary Figure 1. Linear fitting of PS 70k SWNT corona phase data to adsorption site balance with fluorescein sodium and riboflavin.



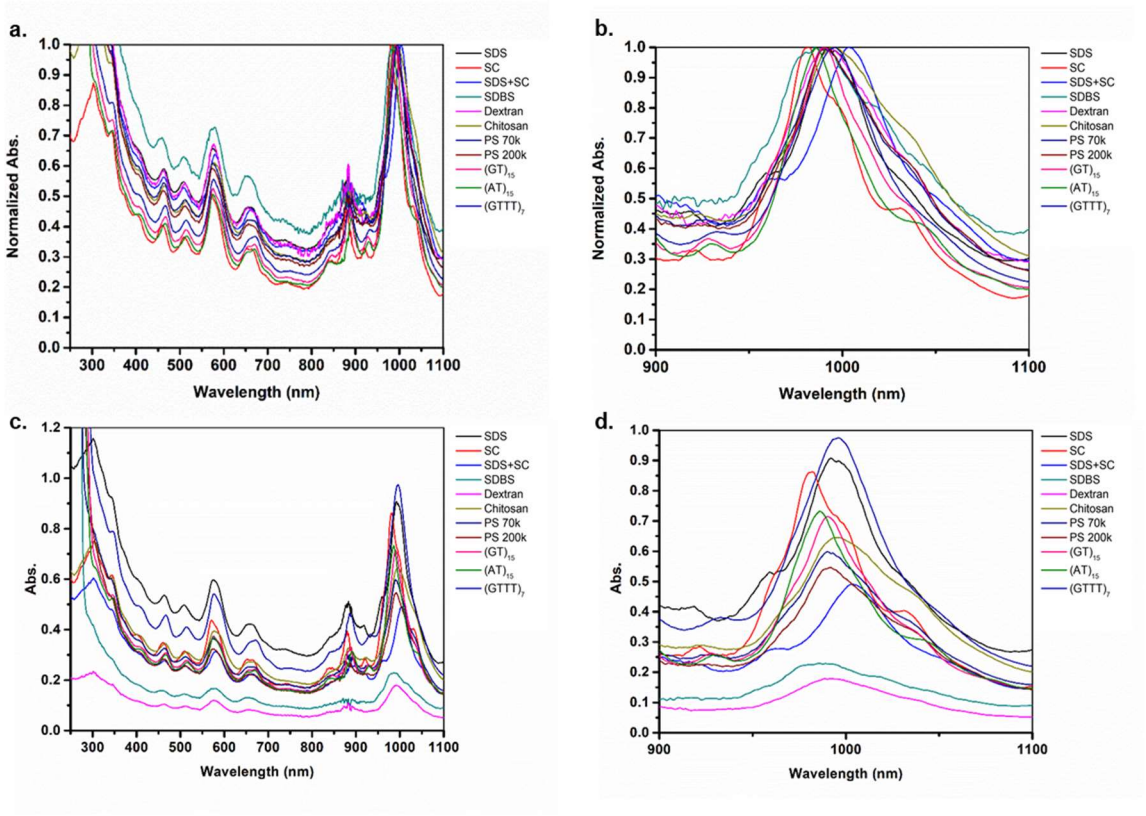
Supplementary Figure 2. Riboflavin emission spectra as a function of added nanoparticle concentration for PS beads (100nm).



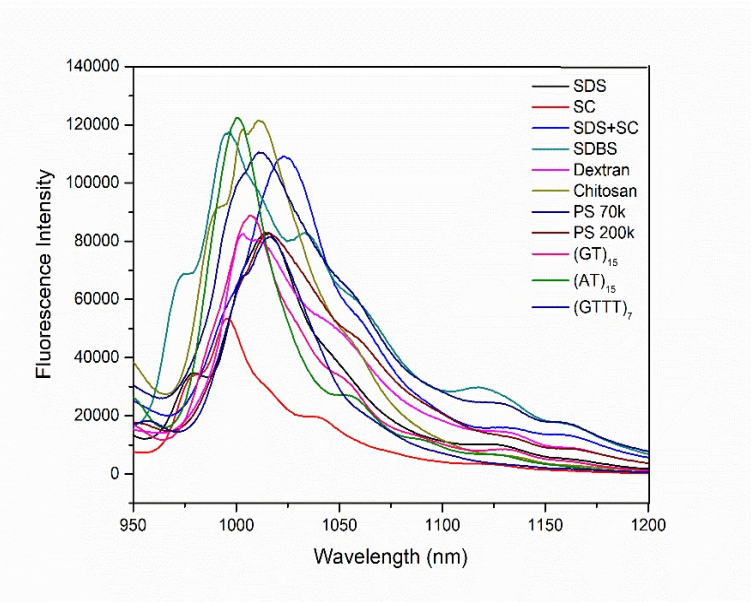
Supplementary Figure 3. Raw data of eleven SWNT corona phases obtained from the plate reader. a. SDS-SWNT b. SC-SWNT c. (SDS+SC)-SWNT d. SDBS-SWNT e. PS 200k-SWNT f. PS 70k-SWNT g. Dextran-SWNT h. Chitosan-SWNT i. $(AT)_{15}$-SWNT j. $(GTTT)_7$-SWNT k. $(GT)_{15}$-SWNT.



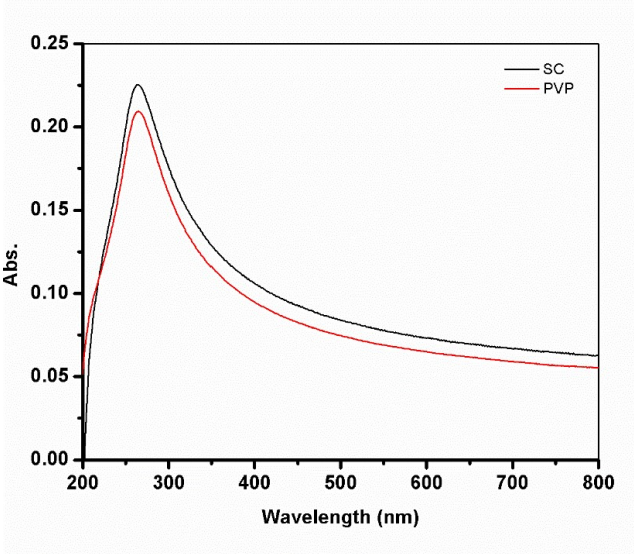
Supplementary Figure 4. Comparison of nIR fluorescence spectrum of SWNT before and after addition of different concentration of fluorescent probes. a. SDS-SWNT b. (SDS+SC)-SWNT c. PS 200k-SWNT d. Dextran-SWNT e. Chitosan-SWNT f. $(AT)_{15}$-SWNT g. $(GTTT)_7$-SWNT h. $(GT)_{15}$–SWNT.



Supplementary Figure 5. UV absorption spectra of eleven SWNT corona phases. a and b. Normalized UV absorption spectrum based on E_{11} peaks near 1000nm. c and d. Unnormalized UV absorption spectrum.



Supplementary Figure 6. nIR fluorescence spectra of eleven SWNT corona phases when excited at 785nm wavelength light.



Supplementary Figure 7. UV absorption spectra of graphene corona phases: SC-graphene and PVP-graphene.