Electronic Supplementary Information

Viscosity sensitive near-infrared fluorescent probes based on functionalized single-walled carbon nanotubes

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Experimental and computational details

Theoretical calculation The twist of a dimethylaniline group anchored on a (6,5) SWCNT was calculated by the density functional theory method using Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009). The geometry optimization was performed with Becke's three-parameter hybrid exchange function and Lee-Yang-Parr gradient-corrected correlation functional and 6-31G** basis set (B3-LYP//6-31G**). The calculation considered one benzene group covalently attached to the nanotube center. No constraints to bonds/dihedral angles were applied in the calculations. All atoms were free for the optimization. The electronic transition energies and corresponding oscillator strengths were calculated with time-dependent DFT (TD-DFT).[1, 2] The S_0 potential energy curve was qualitatively scanned by constrained the optimization at dihedral angels fixed at different values. The excited-state potential energy curve was obtained by calculating the Franck-Condon transition energies for the ground-state optimized structures at fixed dihedral angels using the TD-DFT method. It should be noted that similar methods have been used to calculate the energy level and bandgap information of many other fluorescence molecules with rotatable moieties, for example, *Chemical Physics*, **1985**, 96(1):145-151;[3] *J. Phys. Chem. A,* **1999**, 103, 3969-3980;[4] *J. Am. Chem. Soc.,* **1990**, 112, 6329-6338;[5] *Eur. J. Org. Chem.* **2011**, *4773–4787;*[6] *ChemPhysChem*, **2013**, 14, 1601;[7] *Chem. Eur. J.*, **2013**, 19, 1548.[8]

Diazonium salt synthesis 4-*N, N'*-dimethylaniline-diazonium tetrafluoroborate was synthesized by the following method. 1.5 mL of deionized water and 1 mL of tetrafluoroboric acid solution (48 wt.% in water, Sigma) were added to a round bottom flask, which was then cooled in an ice-water bath. 2 mmol of N, N-dimethylaniline was added to the cooled flask. Then, 4.5 mmol of sodium nitrite dissolved in 1 mL of water was added dropwise under stirring. The precipitates were collected and washed with 200 mL of diethyl ether by filtration. All synthesis procedures and the storage of the salt should be protected from light. The salt was stored at 4 °C, and it should be used within a week.

SWCNT functionalization SWCNTs enriched with (6,5) nanotubes were purchased from Sigma Aldrich and used without further purification. The SWCNT powder was individualized in an aqueous solution containing 1 wt.% sodium dodecyl sulfate (SDS, 99%, Sigma) by tip sonication for 2 hours at 0° C in an ice-water bath (80% amplitude, VCX-130, Vibracell). The homogenized suspension was then ultracentrifuged at 20° C for 3 hours at 180,000 g to remove nanotube bundles and other impurities. The concentration of purified SWCNTs was further diluted with 1 wt.% SDS/H_2O

solution to obtain an absorbance of 0.4 at its E_{11} peak wavelength in a standard 1-cm path length quartz cuvette. According to a previous paper[9], the final SWCNT concentration is approximately 2.2 mg L^{-1}. The diazonium salt was dissolved in H_2O to have a 10 mM solution. Aliquots of the solution were added to the SWCNT suspension at a salt/carbon molar ratio of 1:100. The mixture was allowed to react for 3 days under stirring in the dark.

Spectroscopic characterization Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer in 1-cm light lath quartz cells. The photoluminescence emission (PLE) spectra of SWCNT suspensions were collected on a Horiba NanoLog-3 fluorometer with double-monochromator. A 500 W xenon lamp was used as the excitation source. Raman spectra of the samples were obtained on a Renishaw inVia Raman microscope with 633 nm laser excitation. The solid samples were recovered from the suspensions by ethanol-induced precipitation for Raman measurement. X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-alpha XPS spectrometer with an Al-Kα source. The functional group density was estimated based on the atomic concentration of N determined by XPS and the assumption that each repeating unit of (6,5) nanotube is composed of 364 carbon atom and has a length of ~4.06 nm.

Fluorescence-based ratiometric viscosity determination Water/glycerol mixtures were chosen to study the relationship between the PL intensity and solution viscosity. Various water-glycerol mixtures were prepared by mixing DI H_2O with glycerol (with 0.8 wt.% SDS in all solutions) at different volume ratios (water/glycerol = 9:1; 7:3; 5:5; 3:7 and 1:9). Functionalized SWCNT suspension (2.2 mg L^{-1}) were diluted with a proper amount of 0.8 wt.% SDS glycerol solution before mixing with water-glycerol mixtures at a volume ratio of 1:9. The final concentration of SWCNTs in all solutions was maintained at 0.22 mg L^{-1}. After bath sonication for 5 min, the solutions were kept stationary for 1 hour before their UV-vis-NIR absorption spectra, and PLE spectra were collected. To obtained the correlation between the solution viscosity and the PL intensity, the viscosity of water-glycerol mixtures was measured using an NDJ-7 rotation viscometer under similar conditions.

Cell cytotoxicity by the MTT assay Hela Cells were plated in 96-well flat-bottomed plates at 1×10^5 cells per well, and allowed to grow 12 h before exposure to SWCNTs.[10, 11] Then MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-iphenyltetrazolium bromide) reagent was added for 4 h at 37 ℃ and washed with PBS several times. The absorbance at 570 nm and 690 nm (background signals) was recorded by a microplate reader (Spectra Max M2). The viability of cell growth: Cell viability (%) = (mean of A value of treatment group / mean of A value of control) × 100.

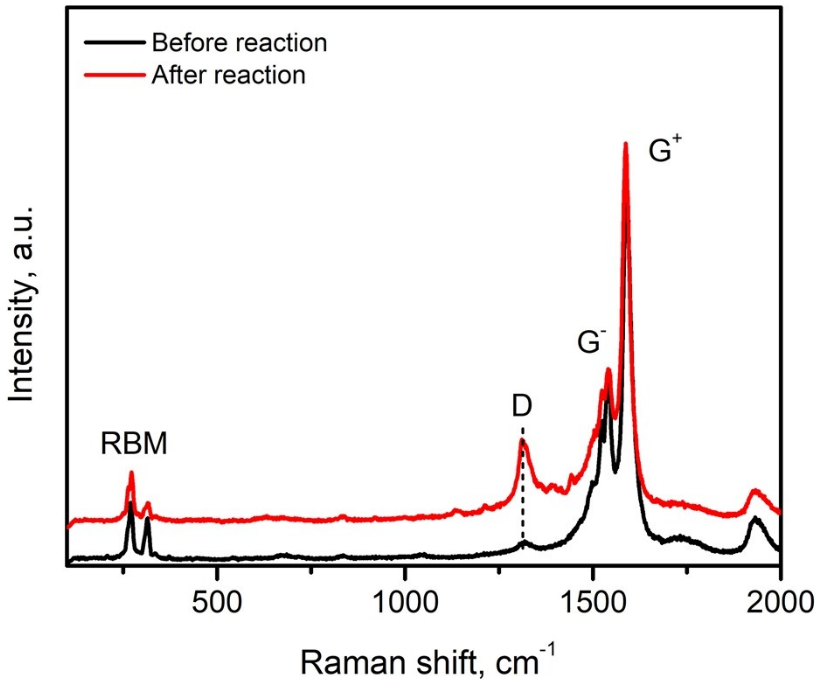

Fig. S1. Raman spectra of (6,5) SWCNTs before and after 4-N, N'-dimethylaniline-diazonium tetrafluoroborate functionalization under 633 nm laser excitation.

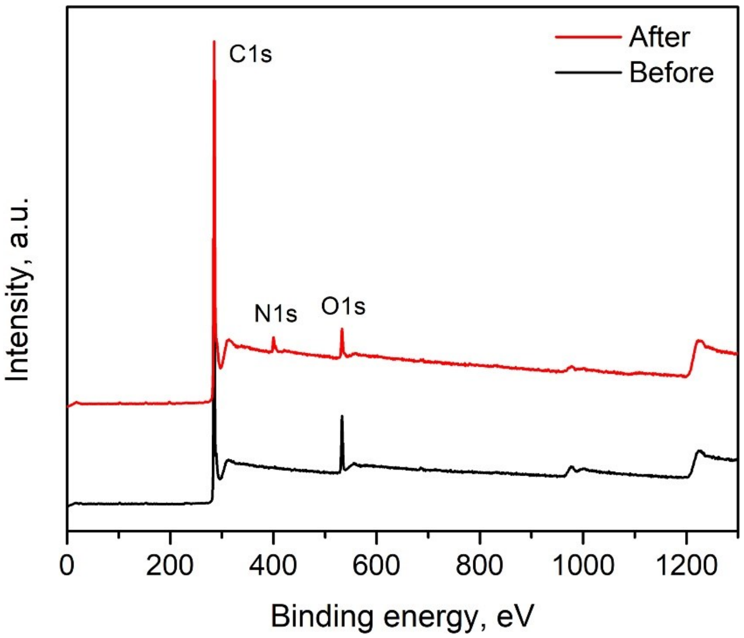

Fig. S2. XPS survey scan of (6,5) SWCNTs before and after 4-N, N'-dimethylaniline-diazonium tetrafluoroborate functionalization.

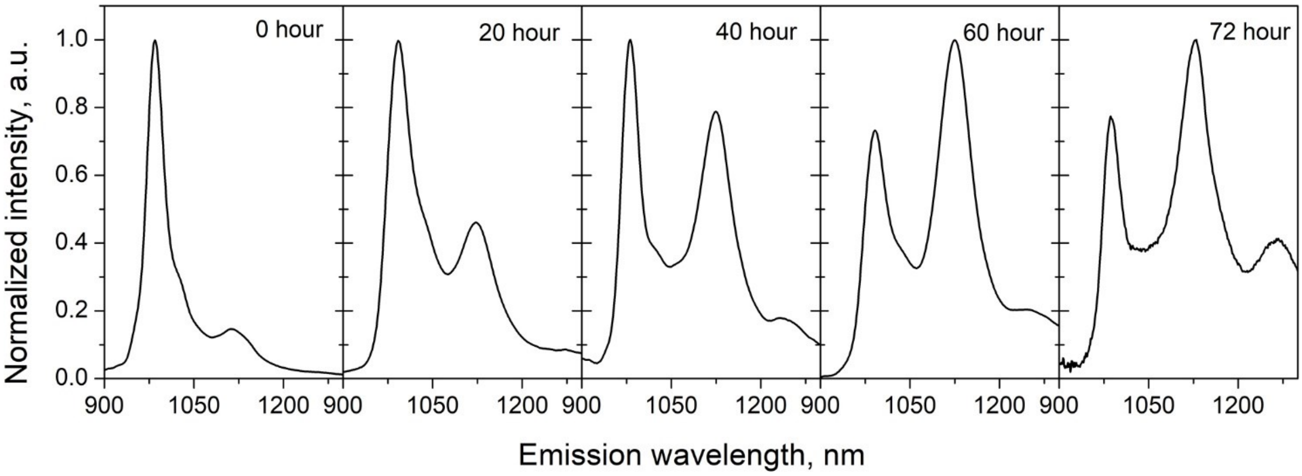

Fig. S3. PL spectra of functionalized (6,5) SWCNTs collected every 20 hours after initiating reaction over 3 days.

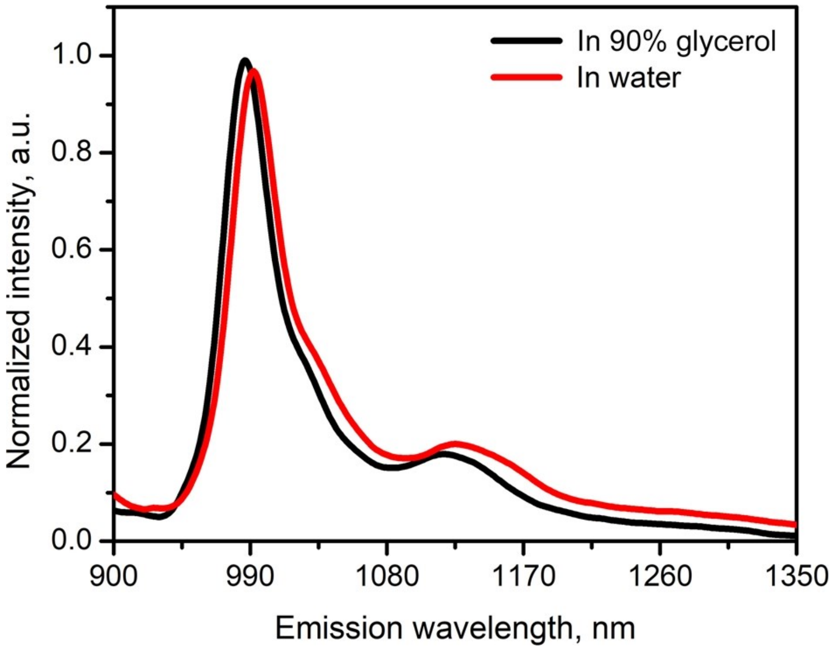

Figure S4. PL spectra of pristine (6,5) SWCNTs in water and water/glycerol (90 vol.%) mixture.

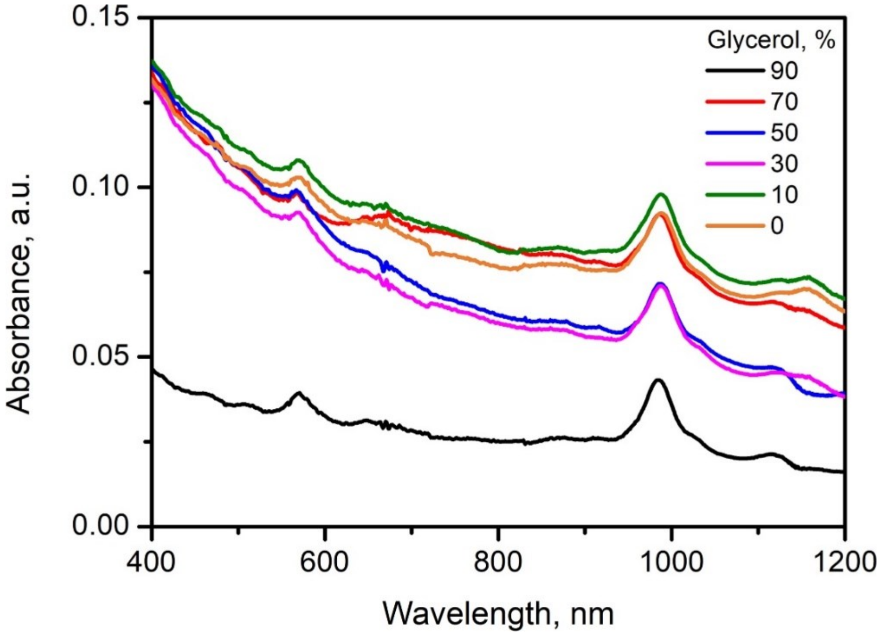

Fig. S5. Absorption spectra of functionalized (6,5) SWCNTs in various water/glycerol mixtures.

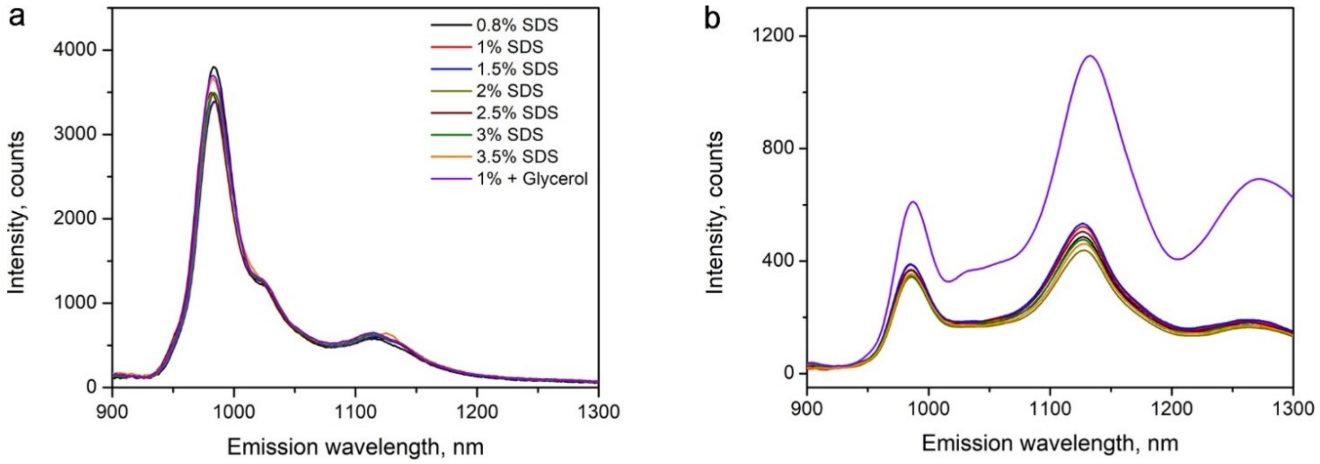

Fig. S6. The effect of SDS concentration on the PL spectra of (a) pristine and (b) functionalized SWCNTs.

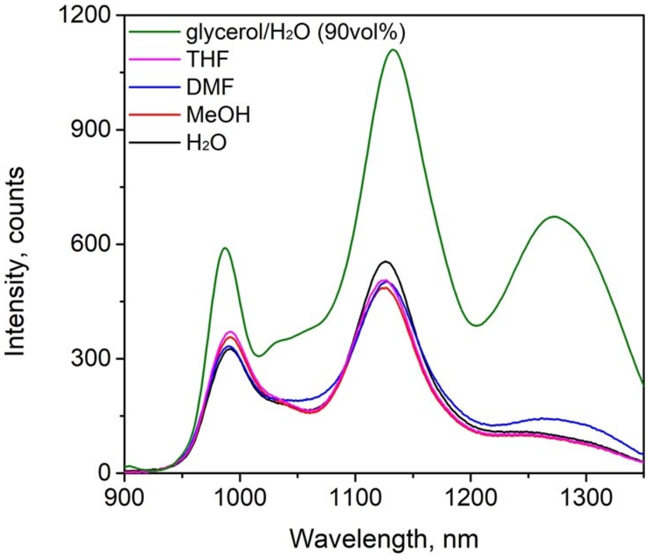

Fig. S7. The effect of the dielectric constant of five different solvent systems on the PL spectra of functionalized SWCNTs at the concentration of 0.22 mg L^{-1}.

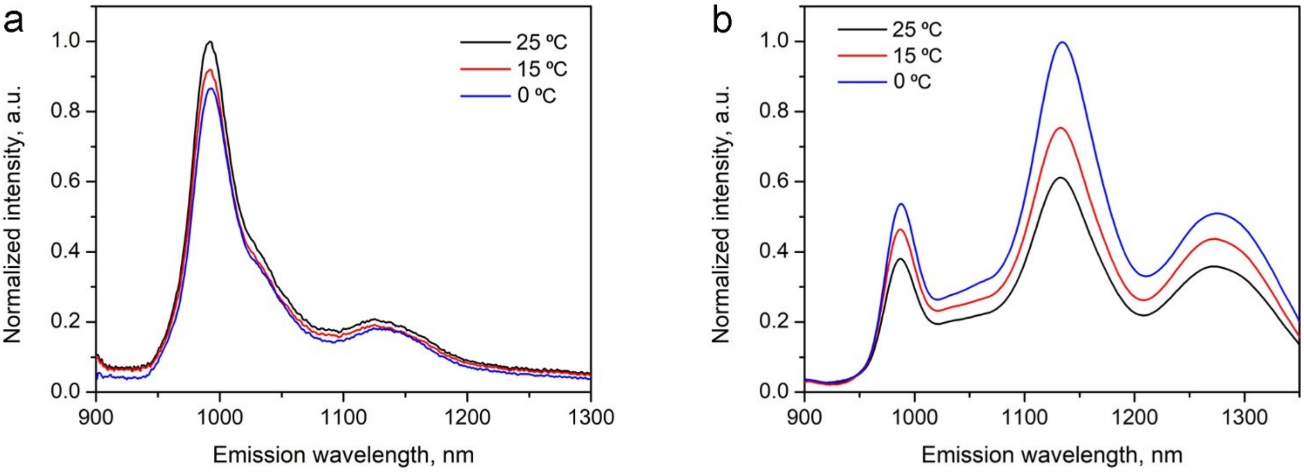

Fig. S8. The effect of temperature on the PL spectra of (a) pristine and (b) functionalized (6,5) SWCNTs in 70 vol.% glycerol-water mixture.

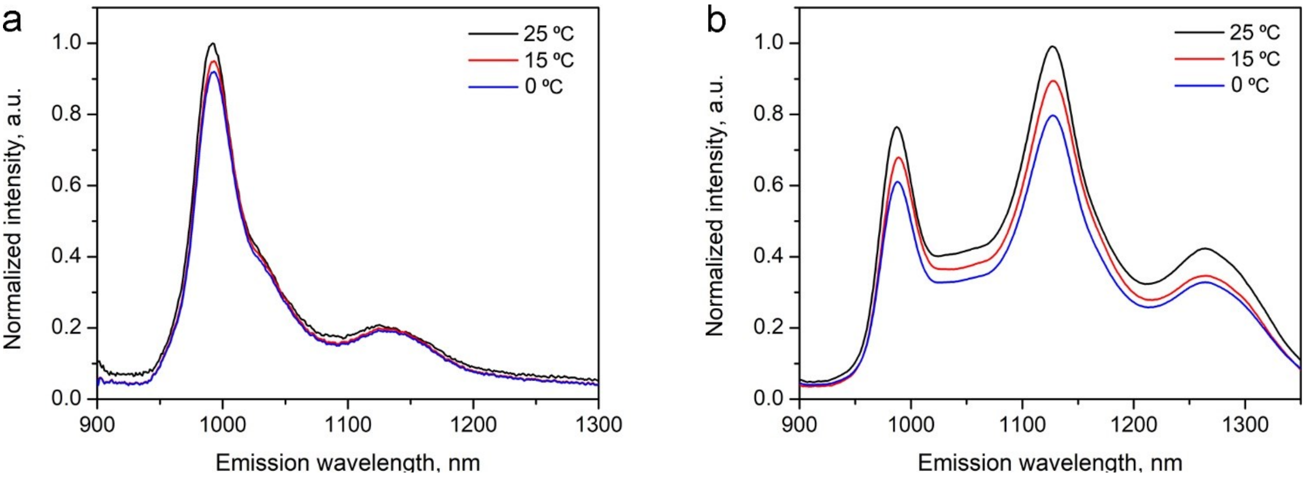

Fig. S9. The effect of temperature on the PL spectra of (a) pristine and (b) functionalized (6,5) SWCNTs in water.

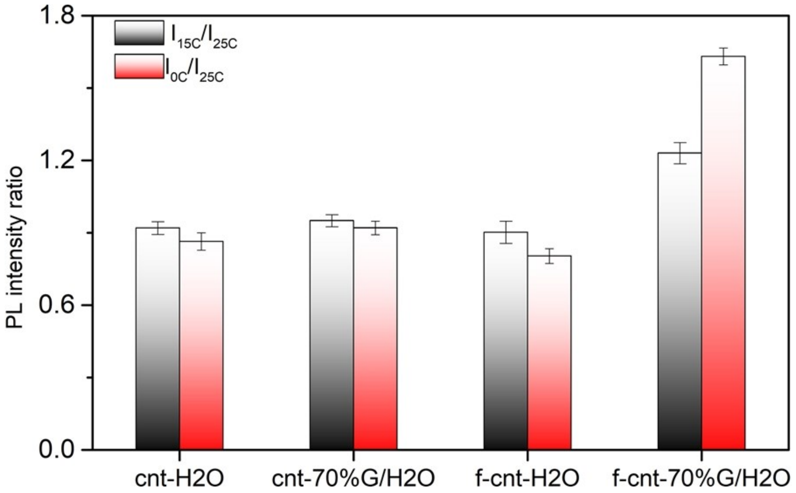

Fig. S10. The relative intensity ratios of pristine and functionalized SWCNTs collected in H_2O or 70 vol.% glycerol-water mixture at 25, 15, and 0 ºC. Results were calculated by taking the average of at least 3 separate tests.

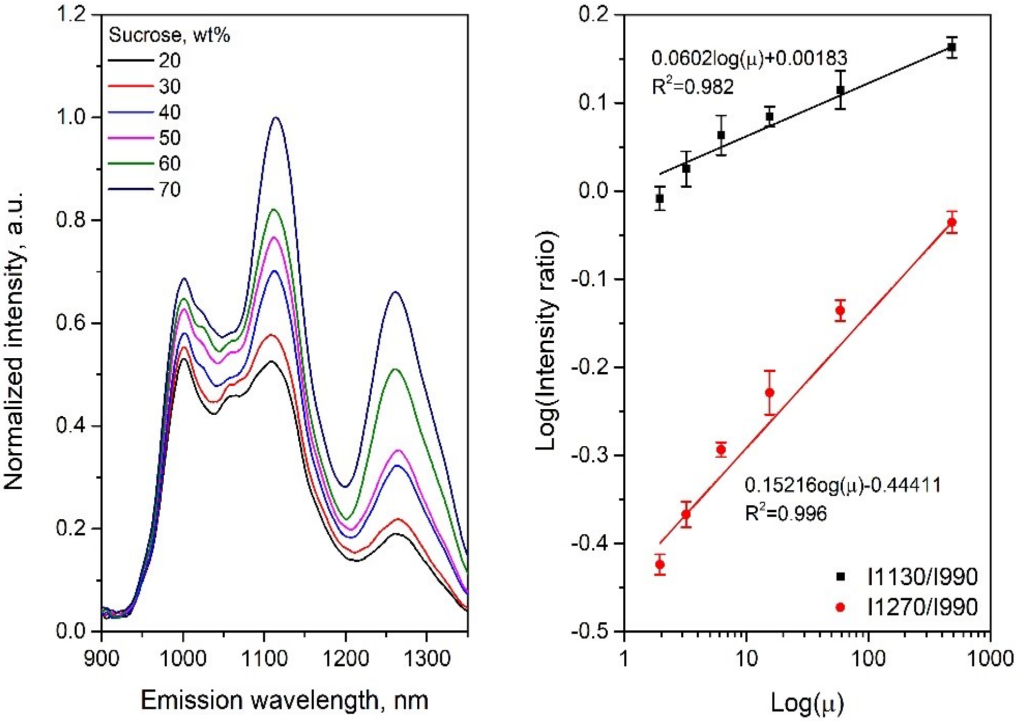

Fig. S11. Various water-sucrose mixtures were prepared by mixing DI H_2O with sucrose (0.8 wt.% SDS in all solutions) at different ratios (sucrose/water = 2:8; 3:7; 4:6; 5:5, 6:4, 7:3).

Table S1. The viscosity of various water/glycerol mixtures and the measured PL intensity ratios of functionalized (6,5) SWCNTs dispersed in these mixtures.

Glycerol, vol%	Temperature, ºC	Viscosity (μ), cP	$\log(I_{1130\text{ nm}}/I_{990\text{ nm}})$	$\log(I_{1270\text{ nm}}/I_{990\text{ nm}})$
0	25	1.00	0.064 ± 0.023	-0.414 ± 0.022
10	25	2.33	0.080 ± 0.020	-0.350 ± 0.032
30	25	11.16	0.127 ± 0.019	-0.275 ± 0.017
50	25	46.02	0.174 ± 0.029	-0.115 ± 0.016
70	25	167.10	0.217 ± 0.012	-0.024 ± 0.023
90	25	585.40	0.271 ± 0.016	0.057 ± 0.016

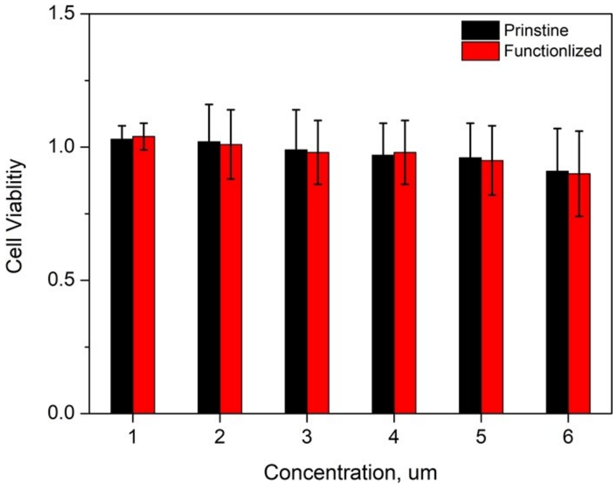

Fig. S12. Cytotoxicity of pristine and functionalized (6,5) SWCNTs at different concentrations on Hela cells. The results were expressed as the mean ± standard deviation (SD) of three independent tests.

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